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*Vacuum Manipulation  
of Volatile Compounds*



# *Vacuum Manipulation of Volatile Compounds*

A LABORATORY MANUAL DESCRIBING  
THE APPLICATION OF HIGH VACUUM  
TECHNIQUE IN EXPERIMENTAL CHEMISTRY

BY

*Robert Thomas Sanderson*

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## Preface

Within the last thirty or forty years, the development of good vacuum pumps, refrigerants, and a glass capable of withstanding thermal shock has made possible an excellent technique for the study of volatile chemical compounds. This is the high vacuum technique, which permits quantitative handling of materials, even in very small amounts, in a very convenient manner.

Despite the large amount of work which has been done in this field, descriptions of the methods and apparatus involved are so scattered in the literature, and so often concealed in experimental details of apparently unrelated chemical work, that it has been difficult for one to begin to use this technique without learning it from another individual. *It is the purpose of this book, therefore, to provide in one place enough practical information to enable an investigator with an average background of scientific training and experience to construct and operate a general purpose high vacuum apparatus for chemical research.*

Although the text is intended primarily as an introduction to vacuum technique, the book should be useful also, as a reference, to those who are already familiar with most of the procedures described. Of especial value should be the lengthy table of vapor pressures of pure compounds.

Vacuum technique as applied to chemistry is, in a sense, an art. There are alternative methods of doing almost everything, and it is expected that others of experience may prefer to practice procedures different from those described herein. There is certainly no intent to imply that the methods given in this book are necessarily the best; it is only claimed that they are workable and should provide a foundation from which an investigator may build and modify as much as desired. Neither is there intent to imply that this book is comprehensive. It is hoped, however, that it contains enough information to fulfill its stated purpose. I shall welcome any suggestions for its improvement.

The present state of development of this vacuum technique is

the cumulative result of the experience of many workers, and it would be impossible to give credit as it is due. However, the contributions of Alfred Stock and his many coworkers, who pioneered in the application of high vacuum to chemistry in their remarkable studies of hydrides of boron and silicon, deserve special mention.

I am indebted directly or indirectly to all the previous workers in this field. An effort has been made to refer specifically to published work, but it has not always been possible to know with certainty where or when or by whom certain procedures were originated. Professors H. I. Schlesinger and A. B. Burg guided my early training in this technique at the University of Chicago, and I gladly record my indebtedness to them. The text has benefited by suggestions from Dr. E. A. Naragon and from Professors H. C. Brown and T. I. Taylor. My wife has been very helpful in the preparation of the manuscript, and my thanks go especially to her and to my brother, R. A. Sanderson, for their loyal encouragement.

R. T. S.

*Fishkill, N. Y.*  
*August, 1948*



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## *Introduction to Chemical High Vacuum Technique*

Vapors diffuse rapidly through a vacuum. This fact is the basis of the high vacuum technique for handling volatile, condensable substances. If a volatile substance is introduced into a closed system from which almost all air and other noncondensable gases have been removed (pressure  $10^{-3}$  mm Hg or lower), its vapor will diffuse rapidly throughout the entire system. It may then be moved quantitatively to any part of that system by cooling that part to a temperature at which the substance exerts a negligible vapor pressure. In other words, the kinetic energy of the molecules of vapor provides the motive power for the transfer, which is made irreversible by removing the kinetic energy at the point of cooling.

In order to make use of vapor diffusion as a means of handling volatile materials, the following are needed:

(1) An enclosed system comprising interconnected apparatus suitable for measuring the properties and studying the reactions of volatile materials, and including means of introducing materials to and removing materials from the system.

(2) Pumps capable of exhausting the enclosed system to the desired high degree of vacuum, and a gage for measuring the residual low pressure.

(3) Refrigerants capable of cooling the materials under study to temperatures at which their vapor pressures are negligible.

With these, it becomes possible to conduct studies in which volatile materials, even in very small amounts, can quantitatively be measured, mixed, separated, moved at will through reaction zones or from container to container, and otherwise manipulated

without loss and without contact with anything but mercury and glass. Chemical reactions and their products can be studied, and such properties as melting point, vapor density, vapor pressure, dissociation pressures, and reaction rates can readily be measured.

All materials which do not react at ordinary temperatures with mercury or Pyrex glass can be manipulated by high vacuum technique if they have vapor pressures at room temperature of at least a few tenths of a millimeter. Compounds that boil (or sublime) at atmospheric pressure up to about 150–200°C are included in this category. Nonvolatile materials may be introduced into the vacuum system by special methods, or they may be synthesized in situ from volatile materials, thereby further extending the scope of application of high vacuum technique.

The high vacuum technique is uniquely suited to the study of materials in small quantities, of the order of a few milliliters of vapor, and to the study of highly reactive materials, such as those spontaneously inflammable in air. It may easily be adapted to the handling of larger quantities, up to 50–100 ml or more of liquid, and for studies involving the synthesis and reactions of compounds containing radio-carbon or other tracer elements the technique can be extremely useful. It is also very convenient for the study of chemical reactions, including biological reactions such as fermentation, which produce gaseous products, since such products are thus quantitatively contained and can be readily handled.

Although it possesses some features uniquely its own, high vacuum technique as applied in chemistry is a composite of a number of separate and otherwise independent procedures and skills. These are elucidated in the following pages in a sequence which is, therefore, necessarily somewhat arbitrary. Only when these parts have been assimilated can a practical understanding of the chemical high vacuum technique as a whole be realized. Consequently, a description of the complete apparatus which is an essential feature of this technique is reserved for the final chapters.

## *Materials of Construction and Operation*

The most important materials involved in the construction and operation of a typical high vacuum system for chemical research are Pyrex glass, mercury, stopcock lubricant, and sealing wax. Gases and vapors handled by the techniques described herein need never come in contact with any other materials, and, if necessary, only momentarily with the last two. A review of the more important properties of these substances is therefore pertinent.

### PYREX GLASS \*

**Chemical and Thermal Properties.** Pyrex laboratory glass (Pyrex brand chemical glass No. 774 of the Corning Glass Works, Corning, New York) is a chemically inactive borosilicate glass of low alkali content, containing no elements of Group II of the Periodic System, and essentially no arsenic or antimony. It is colorless and transparent. When properly annealed, it is reasonably resistant to mechanical shock and remarkably resistant to thermal shock. Both of these properties, especially the latter, are of vital importance in high vacuum work, where breakage may be dangerous as well as extremely wasteful of time and effort. The very low coefficient of thermal expansion,  $32 \times 10^{-7}$  between 19–350°C, permits very rapid temperature changes. For example, properly constructed tubes may be suddenly cooled from room temperature to about –200°C, and as suddenly rewarmed, with reasonable safety.

\* The words *Pyrex* and *glass* will be used synonymously throughout this text, unless otherwise specified.

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The "strain point" for Pyrex is  $510^{\circ}\text{C}$ . This means that Pyrex can be heated under stress for considerable periods of time below that temperature without being appreciably deformed. For ordinary purposes, Pyrex is sufficiently viscous at its annealing temperature,  $560^{\circ}\text{C}$ , to be quite resistant to deformation, and it sometimes can be heated above  $600^{\circ}\text{C}$  for short periods of time without its losing shape. However, unnecessary heating above the strain point should be avoided, since glass thereby develops strains which can only be eased by slow, uniform cooling. Pyrex can be softened sufficiently for bending by the heat of a Bunsen burner flame, but for general glass blowing, the heat of a gas-air-oxygen or gas-oxygen burner is required.

The fabrication of laboratory apparatus from Pyrex glass will be discussed at greater length under the general subject of glass blowing, in Chapter Three, but it can be mentioned here that the relative ease of working Pyrex adds very significantly to its unique value as a material for the construction of high vacuum apparatus for chemical work.

**Strength.** The mechanical strength of Pyrex, or of any glass, is so dependent on the thoroughness of strain removal by annealing, and perhaps also on its previous history, that it is difficult to be very specific about how much force the glass can withstand without breaking. Well-annealed Pyrex under some circumstances has been known to withstand remarkably high pressures, but, where pressure vessels of any material whatever are involved, it is always best to operate with a large factor of safety. Owing to the uncertainties of glass strength, even a very conservative safety factor does not insure perfect safety; therefore *it is well to observe precautions when subjecting glass apparatus to any pressure differential at all.*

However, in general it may be said that properly annealed apparatus made from standard tubing not exceeding 1 inch in diameter can usually be relied upon to withstand internal pressures of 3–5 atmospheres without breaking, and probably will not break even at pressures of about 10 atmospheres. Apparatus of larger dimensions is likely to have less strength.

When subjected to the pressure differential of 1 atmosphere created by evacuation, properly constructed glass apparatus is quite unlikely to collapse. Larger apparatus, such as bulbs of

more than 1-liter volume, is relatively more likely to collapse when evacuated, but the possibility is still not very great. However, glass collapsing under atmospheric pressure may shatter and fly about with surprising force. It is therefore conservatively recommended that any vessels exceeding 300 ml in volume, or perhaps 3 inches in diameter, be enclosed in wire netting or heavy cloth if subject to evacuation, especially where, as in the high vacuum apparatus, the vessels may also be subjected to thermal strains while evacuated.

Apparatus of much smaller dimensions may collapse when evacuated unless it is properly constructed. Even if it is well constructed, mechanical breakage when the glass is evacuated may cause fragments to fly through the air; consequently it is well for the eyes of the operator to be protected when he works with any glass vacuum system.

## MERCURY

This very familiar element would be extremely difficult, if not impossible, to replace in general high vacuum work. Its usefulness is due to both its physical properties and its general chemical unreactiveness.

**Physical and Chemical Properties.** Mercury melts at  $-38.9^{\circ}\text{C}$  and boils at  $356.95^{\circ}\text{C}$ . Its vapor pressure is 0.000185 mm at  $0^{\circ}\text{C}$ , 0.0017 mm at  $24^{\circ}\text{C}$ , and 0.273 mm at  $100^{\circ}\text{C}$ . Its density at  $0^{\circ}\text{C}$  is 13.595.

Mercury is not appreciably oxidized by air or oxygen at ordinary temperatures, but it is slowly converted to the oxide when heated near the boiling point in air. It dissolves many metals, forming amalgams, but not iron or platinum. It is unaffected by alkali. It reacts with nitric acid and with hot concentrated sulfuric acid. Sulfur reacts with mercury, forming  $\text{HgS}$ . Dry  $\text{H}_2\text{S}$  does not affect mercury at ordinary temperatures; if oxygen is present, the sulfide may be formed. Cold aqueous solutions of  $\text{SO}_2$  are without effect.

Mercury is attacked by all the halogens, but only by the more unstable of the hydrogen halides:  $\text{HF}$ , either gaseous or aqueous, has no effect, and the same is true of cold  $\text{HCl}$ , whereas  $\text{HBr}$  reacts slowly when cold and more rapidly when hot, and  $\text{HI}$

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reacts rapidly. Similarly, mercury reacts slowly with relatively unstable organic halogen compounds, such as methyl iodide, from which free halogen may be liberated.

Although mercury is quite inert to most gases and vapors likely to be handled in a high vacuum system, it is well to keep its chemical properties in mind to avoid the extreme inconvenience possible if the inside of the apparatus should become contaminated with mercury compounds.

**Toxicity of Mercury Vapor.** Compounds of mercury are well known to be very poisonous, but the poisonous quality of the vapor of mercury itself is often not adequately appreciated. Since mercury is commonly encountered in the scientific laboratory and is practically indispensable in high vacuum work, the potential hazard involved should be clearly recognized, and therefore it will be discussed in some detail.

The possibility of reaching toxic concentrations of mercury vapor in the atmosphere of a room containing exposed liquid mercury is very real. Mercury has a vapor tension at room temperature of about  $2 \times 10^{-3}$  mm. Since the diffusion of heavy mercury vapor into the air would be expected to be extremely slow, equilibrium concentrations would probably rarely be approached in the presence of normal ventilation. However, it is generally agreed that as little as 0.25 mg of mercury vapor per cubic meter of air is dangerous to health, and this is only about  $\frac{1}{70}$  of the room temperature equilibrium concentration. In fact, during the recent war, the American Standards Association<sup>1</sup> set 0.1 mg of mercury per cubic meter of air as an upper limit for daily exposure not exceeding 8 hours. This is about  $\frac{1}{200}$  of the equilibrium concentration.

At least two factors have made it difficult to determine the degree of toxicity of mercury vapor in the air. First, there are, very probably, appreciable differences in individual susceptibility to mercury poisoning, and, second, chronic mercurial poisoning may be very difficult to diagnose because of its insidious property of causing symptoms which are not specific or unique. Indeed, it seems possible that some of the very workers who

<sup>1</sup> P. A. Neal and F. H. Goodman, *Occupational Hazards*, 5, No. 7, pp. 10-11, 24 (1943).



regard the mercury vapor hazard as practically negligible may themselves unknowingly be among the victims.

It is claimed that continued inhalation of very small concentrations of mercury vapor may cause psychic disturbances such as irritability and timidity, as well as such other symptoms, difficult to diagnose, as pallor, anemia, tremors, various digestive disturbances, and occasional shifting neuralgic pains in the joints and in the chest. In the mouth, this poisoning may be manifested by a coppery discoloration of the mucous membranes, a dark

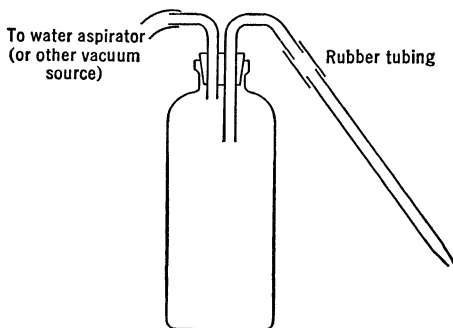


FIG. 1. Collector for spilled mercury.

line on the gums, excessive salivary flow, and excessive tooth decay. Knowledge of these symptoms, and of the degenerative organic changes which occur gradually during long exposure to mercury vapor, makes it difficult to sympathize with the careless indifference which permits dispersion of mercury over laboratory benches and floors. There is never any need to risk the hazard of mercury poisoning.<sup>2</sup>

**Collecting Spilled Mercury.** As will be seen presently, high vacuum apparatus can be so constructed that there is no exposure of mercury to the atmosphere. Spilled mercury can be picked up with a device like that shown in Figure 1. It is desirable to

<sup>2</sup> For further details on this subject, see R. R. Sayers, *U. S. Bur. Mines, Repts. Invest.*, No. 2354 (1922); J. A. Turner, *U. S. Pub. Health Repts.*, **39**, 329-331 (1924); A. Stock, *Z. angew. Chem.*, **39**, 461-466 (1926); *ibid.*, 984-989 (1926); C. F. McCarroll, *U. S. Bur. Mines, Repts. Invest.*, No. 3475 (1939); M. Shepherd, S. Schuhmann, R. H. Flinn, *et al.*, *J. Research Natl. Bur. Standards*, **26**, 357-375 (1941), Research Paper No. 1383; A. Stock, *Ber.*, **75B**, 1530-1535 (1942).

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keep such a device assembled and on hand, with a long tube for connecting it with a source of vacuum such as a water aspirator. When mercury has splattered into tiny droplets on the floor, as it usually does, the task of removing it can sometimes be facilitated by pouring water over it to make it easier for the droplets to combine when scraped together before they are drawn into the container.

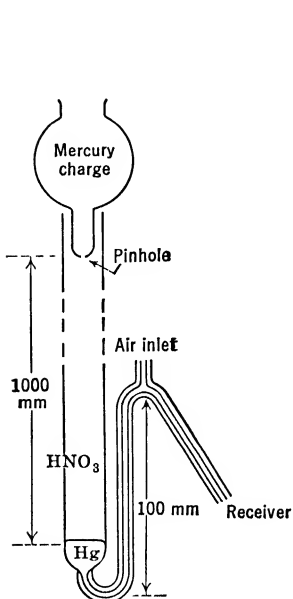


FIG. 2. Mercury scrubber.

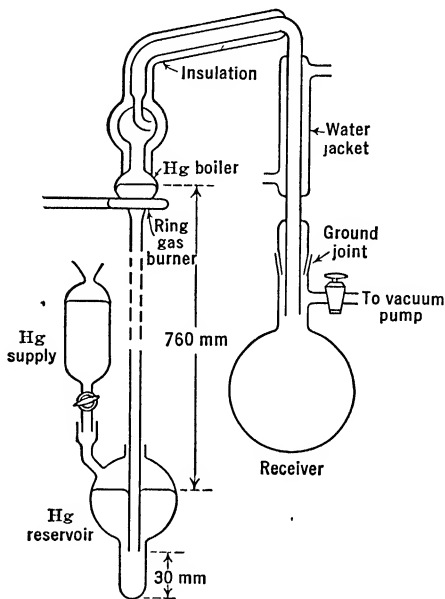


FIG. 3. Mercury still.

**Purification.** Only very pure mercury should be used in the high vacuum apparatus. Ordinary mercury may be contaminated with surface impurities like grease or oil and dirt, and with dissolved impurities such as other metals.

Mercury may be cleansed of grease by washing with an appropriate solvent, and of dirt by letting it run through a pinhole and straining it through cloth.

There are various ways of removing dissolved metals. Bubbling air through the mercury converts metals such as the alkalis, zinc, copper, and lead to oxides, which separate as a surface scum which can be removed by straining or "pinholing." Perhaps a

better method of removing the last traces of the same metals is washing with 5–10% nitric acid. One way to accomplish this is to allow the mercury to fall through a tiny hole into a column of acid, forming therein a fine mercury spray which settles to the bottom of the tower and continuously flows out, as shown in Figure 2.

Traces of the noble metals and tin may then be removed by a vacuum distillation. Numerous continuous stills have been devised for this purpose; one is shown in Figure 3. This still provides for maintaining the proper mercury level in the boiler semi-automatically by continuous atmospheric pressure feed from a reservoir, which in turn may be continuously supplied from a dropping funnel. Minor adjustments of the mercury level in the boiler may readily be made by raising or lowering the reservoir. Once initial level, feed, and heat adjustments have been made, this still may be operated indefinitely with very little attention.

In summary, mercury of unknown purity can usually be purified satisfactorily for use in a high vacuum apparatus by (1) washing with pentane or similar light solvent, (2) running through a tiny hole, (3) washing thoroughly with 5–10% nitric acid, and finally (4) vacuum distilling.

## STOPCOCK LUBRICANT

An ideal lubricant for stopcocks and other ground-glass joints to be used in high vacuum work would have the following properties:

- (1) Very low vapor pressure (preferably below  $10^{-6}$  mm).
- (2) Excellent workability. (It should maintain a continuous film permitting no possibility of leakage despite turning of the joints. It should not become hard and rigid on long standing, thus immobilizing or "freezing" the joint.)
- (3) Chemical inertness. (It should be sufficiently stable toward oxidation so that its properties are not impaired by long standing in contact with air. It should not react chemically with any of the gases or vapors which may come in contact with it.)
- (4) Nonsolvent properties. (It should not absorb or dissolve gases or vapors which may come in contact with it, since, besides

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interfering with the functioning of the lubricant, these are then released very slowly into the vacuum system, making it impossible for a long time to produce or maintain a high vacuum.)

(5) Flow resistance. (It should not flow appreciably under gravity.)

These properties represent ideals which unfortunately do not appear to be attained by any available lubricant. Therefore it becomes necessary to clean and regrease all ground joints in a vacuum system periodically. Since this task always involves admitting air to the system with subsequent delay in obtaining high vacuum again, it is advisable to use the best available grease.

Among numerous compositions devised or proposed for lubricating and sealing joints in high vacuum work, the Apiezon greases "L" and "M" appear to be superior. These are highly purified hydrocarbon greases having suitably low vapor pressure<sup>3</sup> and relatively good working characteristics. They are, of course, capable of absorbing organic vapors, and they do tend to become somewhat less workable with use and long exposure to air. It is advisable, particularly for infrequently used joints having large lubricated surfaces, to move the joints a little every day to help prevent "freezing," or at least to help in detecting incipient lubricant failure.

Other types of commercially available stopcock lubricants which are especially recommended by the manufacturer for high vacuum work will also be found fairly satisfactory.\*

A number of investigators have described modifications of Ramsay grease, composed of petrolatum, paraffin, and unvulcanized rubber, as useful for vacuum work.<sup>4</sup>

<sup>3</sup> C. R. Burch, *Proc. Roy. Soc. (London)*, **A123**, 271 (1929); G. Seydel, *Z. tech. Physik*, **16**, 107–109 (1935). Obtainable from James Biddle Co., Philadelphia, Pa.

\* For example: Vacuscal, light and heavy, from Central Scientific Company, Chicago, Ill.; Celvacene, light, from Distillation Products Co., Rochester, N. Y.; and Silicone greases from Dow-Corning Corp., Midland, Mich.

<sup>4</sup> E. G. R. Ardagh and A. L. Davidson, *Can. Chem. Met.*, **9**, 137 (1925); C.A., **19**, 2410 (1925); A. T. Sveshnikov, *Zavodskaya Lab.*, **5**, 503 (1936); C.A., **30**, 5837 (1936); B. Bruns, V. Sadovnikov, and N. Kolesnikov, *J. Tech. Phys. (U.S.S.R.)*, **7**, 964–966 (1937); *Chem. Zentr.*, **1938**, II, 1089; C.A., **34**, 4892 (1940).

The hydrocarbon greases are fairly resistant to the lower alcohols and acetone, but they tend to dissolve hydrocarbon vapors appreciably. When lubricants less affected by hydrocarbons are needed, use may be made of either organic, nonhydrocarbon greases or inorganic lubricants.

In the first class are compositions containing highly oxygenated organic materials such as starch, sugars, and glycerin or polyether glycols. For example, a lubricant said to be quite unaffected by a large number of organic compounds, including hydrocarbons and chlorohydrocarbons, is made <sup>5</sup> by heating a mixture of 25 g of anhydrous glycerin, 7 g of dextrin, and 3.5 g of pure *d*-mannitol just to boiling, then cooling to room temperature. This is, of course, affected by water, alcohols, aliphatic acids, and some amines. An improvement on the above composition is said <sup>6</sup> to be obtained by substituting a medium viscosity polyvinyl alcohol for the dextrin. The revised composition is made by mixing glycerin with 1–3 per cent of polyvinyl alcohol and 15–20 per cent of mannitol at room temperature, then heating at 130°C and stirring until dispersion is uniform and complete. This grease was found to absorb much less diethyl ether or hydrocarbon vapors than did Apiezon “M.”

Another composition of this general type is made by preparing first a solution of 7.5 g of Celanese (cellulose acetate) in 45 g of tetraethylene glycol and then heating and stirring it for 4 hours at 140°C until it is homogeneous.<sup>7</sup> Thirty grams of citric acid is then heated to 190°C, and the above solution is added, the entire mixture being heated at 180–190°C for 90 minutes. The mixture is then transferred to a dessicator, and water is removed by evacuation.

The newer developments in synthetic lubricating oils and high polymers open up a vast number of new possibilities for making superior ground joint lubricants for special purposes.

The second class of nonhydrocarbon lubricants comprises inorganic materials. Metaphosphoric acid,  $\text{HPO}_3$ , has been used as a stopcock lubricant, but it may contain moisture and thus

<sup>5</sup> C. C. Meloche and W. G. Frederick, *J. Am. Chem. Soc.*, **54**, 3264–3266 (1932).

<sup>6</sup> I. E. Puddington, *Ind. Eng. Chem., Anal. Ed.*, **16**, 415 (1944).

<sup>7</sup> W. H. Pearson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 415 (1944).

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give a slight vapor pressure. Ground joints have been silvered and then lubricated<sup>8</sup> with a mixture of 5 g of solder, 5 g of Wood's metal, 2.5 g of zinc, and 80 g of mercury. Finely powdered graphite makes a fairly good lubricant for ground joints, but it is not completely gastight. It can be used successfully in conjunction with a mercury seal.<sup>9</sup>

A discussion of lubricants can perhaps best be concluded by stating that in general, wherever in high vacuum work the choice of lubricants presents a chemical problem, it is better to eliminate the need for lubricants altogether so far as possible. Methods of doing this are described in the discussion of valves, Chapter Seven.

### VACUUM WAX

Wax is useful in high vacuum work for temporary sealing of cracks and pinholes in glass, and for making temporary seals, as for connecting weighing bulbs to the vacuum apparatus.

A number of different compositions of vacuum wax have been developed, of which perhaps the best known are picein and deKhotinski cement. Of these two, picein seems preferable since it is somewhat easier to work with and it has a lower vapor pressure, well below  $10^{-3}$  mm.<sup>10</sup>

Picein is a black hydrocarbon wax which is fairly hard but not unduly brittle at ordinary temperatures. It softens over a considerable temperature range, becoming quite plastic at 50°C, and, although in the fluid state it is too hot (about 80°C or higher) to touch, it is quite pliable at temperatures at which it can be readily handled. It may be softened in a carbon flame of a gas burner; it does not inflame unless heated well above its fluid point. When quite soft, it adheres very well to glass or to almost any other solid, dry surface, forming a vacuum-tight seal. A better seal is created if the glass or other surface is warmed before the wax is applied. When fairly fluid, picein sticks very well also to dry fingers, but it can be molded easily with moist fingers without sticking. It may be very simply re-

<sup>8</sup> W. A. Boughton, *J. Am. Chem. Soc.*, **52**, 2421 (1930).

<sup>9</sup> For example, see L. S. Echols Jr., *Ind. Eng. Chem., Anal. Ed.*, **10**, 527 (1938).

<sup>10</sup> R. M. Zabel, *Rev. Sci. Instruments*, **4**, 233-234 (1933).

moved completely from glass or other surfaces by softening with a flame, wiping off the bulk with a dry cloth, and wiping the last traces away with a cloth moistened with carbon tetrachloride, in which it is very soluble.

At temperatures below 0°C, picein becomes very brittle and is apt to shatter; it is not a suitable sealing material at very low temperatures.

Because of its solubility in organic solvents, particularly hydrocarbons and chlorohydrocarbons but not alcohol, it is not suitable for uses involving more than momentary contact with such organic vapors.

DeKhotinsky cement, a shellac composition, is more resistant to organic solvents than picein. Shellac in general is a very useful base for sealing compositions. When mixed with liquids of very low volatility, such as dibutyl phthalate, it gives materials useful for high vacuum seals of considerable strength.

Other waxes of suitably low vapor pressure may of course be used. One of the lowest vapor pressure waxes is Apiezon Wax "W," which melts at 70°C and must be heated to 180°C before its vapor pressure reaches  $10^{-3}$  mm.<sup>11</sup>

Seals which must hold at elevated temperatures may be made from silver chloride, which melts at 455°C. It must be cooled slowly after application to prevent cracking. It may be removed by dissolving in sodium thiosulfate solution.

<sup>11</sup> J. Strong *et al.*, *Procedures in Experimental Physics*, Prentice-Hall, Inc., New York, 1938, p. 557.

## *Glass Blowing*

To work effectively with the high vacuum technique, it is practically essential to be able to blow glass. Even if a professional glass blower is available to construct the more intricate parts of the apparatus, it is very desirable for the operator to know at least how to make minor repairs and to make simple seals.

Glass blowing, like most manual skills, may be learned partly by watching an expert at work and by reading instructions, but, to attain proficiency, there is no substitute for actual practice. It is hoped that the following may be of assistance.

### EQUIPMENT

For most of the work required in constructing and operating a glass high vacuum system, a single gas-oxygen hand torch will be adequate. Such a torch comes equipped with two or three different sizes of nozzles for different sizes of flames. It provides a quiet, blue flame when the proper amount of oxygen is used. By adjustment of the gas and oxygen valves, the flame from any one nozzle may be varied from a very small, sharp point to a fairly broad brush. The torch may be clamped to a stand to serve as a stationary burner, or held in the hand for work on stationary apparatus.

An ordinary commercial-type oxygen cylinder, equipped with a high and a low pressure gage and a reducing valve capable of regulating the oxygen pressure smoothly at 5–10 pounds, will serve very well as a source of oxygen to operate the burner. About 7 pounds oxygen pressure is ample for all but the largest flames. As a safety precaution, it is suggested that a section of noncombustible tubing such as glass be inserted in the oxygen feed line from the cylinder to the burner. This section should



help prevent a fire from reaching the cylinder, in case the oxygen feed line should accidentally be ignited, as, for example, by a piece of hot glass.

Professional glass blowers make use of a variety of hand tools to assist in the shaping of glass, but for ordinary purposes very few are sufficient: a small, sharp three-cornered file or a glass knife, a pointed carbon rod about  $\frac{1}{4}$  inch in diameter for flaring open ends and shaping hot glass, and a pair of tweezers for pulling off hot pieces of glass. None of these is absolutely essential except the file or knife.

At the temperature required for blowing, Pyrex imparts an intense, yellow-white light to the burner flame which is uncomfortably bright for the eyes. Ordinary dark glasses give protection from the light but make it difficult to see that part of the glass which is not at a glowing heat in the flame. This problem has been admirably solved by a special didymium glass (Corning 512), containing a mixture of the rare earths neodymium and praeosodymium, which is capable of absorbing most of the brilliant yellow sodium light but not the other visible rays. A pair of glass blower's goggles made from this glass is strongly recommended.

## MAKING APPARATUS FROM GLASS

**Cutting Tubing.** Glass tubing up to about  $\frac{3}{4}$  inch in diameter is easily cut by making a small file scratch, the sharper the better, at the place to be cut, and attempting to bend the tubing away from the scratch while simultaneously trying to pull the tubing apart. This is a simple procedure when both sides of the tube to be cut are movable, but, when one side is rigid, much greater care is required lest, when the desired piece breaks off suddenly, the rigid part be broken also as a result of the sudden release of stress. Where one or both sides of the desired cut are rigid, it is better to accomplish the break by a sharp, light tap at the point opposite the file scratch. Moistening the scratch before applying the stress will often assist in forming a smoother break.

Tubing of larger diameters may be cut by heating the file scratch by application of a hot glass rod, and then touching the heated scratch with a moist cloth, which causes the glass to crack

in two. This cutting may be facilitated by extending the scratch all the way around the tube. When many such cuts must be made, it is better to use a piece of resistance wire which can be wrapped tightly around the tubing at the desired point and heated electrically. After heating, the wire is quickly removed, and the hot area is lightly brushed with cold water.

It sometimes happens that one side of the desired cut is too short to permit application of enough leverage for breaking. In such a case, or when one portion of the apparatus may be too fragile to risk breakage through sudden release of stress, it may be better either to crack off the desired section thermally, or to melt the glass at the point where cutting is wanted, pull it in two, and blow out the closed end, as will be described in following paragraphs.

**Manipulating Glass in a Flame.** Even though the coefficient of thermal expansion of Pyrex is very small, it is real, and definite strains are set up whenever the glass is subjected to a sharp temperature differential. Such temperature differentials occur whenever the glass is held in a flame. Ordinarily the strains created when tubing of small diameter is suddenly exposed to the heat of a gas-oxygen torch are not sufficient to cause fracture of the glass. However, tubing larger in diameter than 2 cm, or bulbs, or previously worked apparatus, or apparatus containing ring seals should be heated slowly and cautiously to the desired temperature for working; the heat should be distributed carefully over the entire area surrounding the spot to be worked and tapered to the adjacent glass through a distance of 2–3 cm, so that the temperature gradient is gradual. With a stationary flame, this will involve deft manipulation and smooth rotation of the glass to obtain uniform heating on all sides. With a moving flame and stationary apparatus, the burner must be moved smoothly and fairly rapidly over the area.

All glass-working operations which require part of the glass to become so fluid that the glass can no longer support its own shape demand considerable manual dexterity. The problem of manipulating a piece of glass which has been heated to softening at one point is practically one of holding two separate pieces of glass, one in each hand, very close together but not touching, and rotating them and moving them about in all directions with-

out allowing their relative positions to change in the slightest degree. For the average worker, this is the most difficult part of glass blowing; it requires practice long after the methods are thoroughly understood.

When the size and shape of the apparatus permit, it is usually convenient to hold one hand on each side of the place to be heated, with the left hand palm down and the right hand palm up. This position permits coordinated rotation of the glass in the flame and facilitates bringing the right-hand end of the glass to the mouth for blowing.

Although uniform heating is essential for production of the best and smoothest seals and bends, the manual dexterity required, as pointed out above, usually is developed only after long practice. Lacking this skill, one will usually find it much easier to work only one side of a joint or seal at a time, so that the other side remains stiff enough to impart the necessary rigidity and support to the whole. With care, very serviceable, although perhaps less esthetic, seals can be made by this procedure. If the tubing being sealed by this method is large, it is important to keep the whole joint fairly warm, by frequent application of the flame to the cooler side, to avoid setting up thermal strains which will break the joint by cracking before it is complete.

**Annealing.** Glass is not a crystalline material, but nevertheless its molecules do orient themselves to give the glass a rather definite structure. Glass which is most free from internal strains is that which has been cooled from the mobile liquid state most uniformly, so that all the molecules have together gradually lost their freedom of orientation. There is only one way in which glass can be cooled uniformly, and that is, slowly. Otherwise the surfaces must cool more rapidly than the interior, since thermal conduction through glass is very slow.

The process of eliminating structural strains in glass is thus a two-step process: first, the glass is heated to a temperature at which the molecules are sufficiently free to orient themselves with respect to each other; second, the glass is cooled very slowly. This process is called *annealing*.

All parts of glass apparatus which have been heated and worked should be annealed to ease the inevitable internal thermal strains. Complicated apparatus such as that containing ring

seals, and all apparatus containing thick glass, especially where the transition from thick to thin glass is abrupt, may develop such forceful strains, through uneven heating while working, as to shatter or crack spontaneously on cooling, unless annealed. Simpler apparatus, or simpler seals, are usually in no danger of actually cracking spontaneously if poorly annealed, but the seals may have much less mechanical strength and resistance to subsequent thermal shock.

Obviously apparatus cannot be heated to the softening point without becoming deformed, unless it is supported against gravitational and other stresses. However, at temperatures where the resistance to deformation by stress is still high, the molecules of glass are sufficiently mobile to permit slow easing of internal strains by reorientation. Therefore it is feasible to remove most of such strains from glass apparatus by heating it to about 560°C and allowing it to cool very slowly. This can be done best in a special annealing oven in which the heating and cooling can take place over a period of several hours. Even at room temperature, glass can be deformed by stress applied continuously over a long period of time; consequently it is not surprising to find that heavy apparatus may become distorted by gravity in an annealing oven at temperatures at which the deformation of lightweight apparatus or apparatus which can be well supported is negligible within the required period of time.

The conditions provided by an annealing oven can hardly be approached when only a gas-oxygen flame is available for annealing. Nevertheless, a fairly satisfactory annealing job can be done, particularly with small work, by using only the burner. This is fortunate, not only because annealing ovens are scarce and expensive, but also because it would obviously be quite impractical to anneal most of the assembly joints in a high vacuum apparatus in an oven.

To anneal with a gas flame, the burner is adjusted to a large, bluish, brush-shaped flame and the whole area around the part which was worked is reheated, cautiously at first. The most important precaution is to heat this area uniformly by rotating the glass and shifting it about in the flame, rapidly and deftly. Since it is usually not practical to heat the entire piece of apparatus, the next best procedure is to taper the temperature gradu-

ally from the cold glass to the worked section. A tapering distance of approximately twice the cross section of the worked section is suggested. The sodium flame is a good indicator of the proper temperature, as it begins to appear at the temperature of incipient softening. (*Note:* Do not wear didymium goggles while annealing.)

The worked area and its immediate vicinity should be kept at a temperature just below softening, with the adjacent glass diminishing in temperature gradually as the distance from the worked area increases, for perhaps a minute, and then cooling should be begun by very slowly diminishing the oxygen supply, thus decreasing the intensity of the heat. The most important part of the cooling process is the initial part. For best results this should take a few minutes, but small and simple seals can be annealed satisfactorily in a much shorter time. When the glass has become quite rigid, further cooling, even if not uniform, will not set up serious permanent strains. Therefore, when the flame has been gradually made less intense, Pyrex is already well annealed by the time the oxygen has been cut off completely, and only the yellow carbon flame is left. Some workers advocate continuing the heating in the carbon flame until the glass is uniformly coated with carbon; the value of this procedure with Pyrex seems questionable.

**Bending Tubing.** Pyrex tubing of small diameter may be very successfully bent after it has been warmed over an ordinary Bunsen burner with a wing top. This gas-air flame is not hot enough to soften Pyrex for blowing, but it is quite satisfactory for bending. It is recommended that this method be used whenever possible, as it is by far the simplest way of producing neat bends.

The broadest brush flame attainable with an ordinary gas-oxygen hand torch is not broad enough to heat tubing over a sufficient length and uniformly enough for smooth bending, and careful manipulation of the glass is therefore required. With practice, smooth bends may be made over such a burner, even in fairly large tubing. However, unless the bends are very gradual, the inner side tends to kink or cave in as the glass is bent. The resulting imperfections may be smoothed out by stoppering

one end of the tube, heating the imperfect spot to red heat, and blowing gently in the open end.

Acute bends tend to thin out the glass on the outside and crowd it together on the inside of the bend. Although such bends may be made smoothly and without too uneven distribution of glass by heating a considerable length of the glass so that it is quite fluid, and blowing while bending it, such operations require more than ordinary skill. It is much simpler to avoid this difficulty by sealing two separate pieces together at the desired angle.

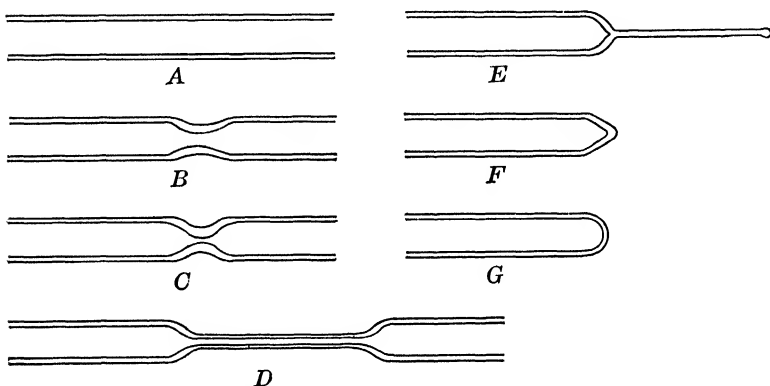


FIG. 4. Making a closed end.

**Making Closed Ends.** The procedure for closing the end of a section of glass tubing is illustrated in Figure 4. The tubing is rotated smoothly in a small, hot flame, so that only a narrow section is heated. The glass tends to shrink toward the hottest part of the heated section, and thicken there, as shown in *B* and *C*. This shrinking is permitted by allowing the two parts of the tube to approach each other slightly. When the glass has shrunk and thickened to the point where the bore is almost or completely closed, as in *D*, the glass is removed from the flame, the two sections are pulled apart several inches, and the intermediate rod is broken when cool, only a stem to be used as a handle, as shown in *E*, being left. The closed end is then rotated in the flame to heat the thickest part of the glass, which is then pulled away from the end until just enough glass remains to make a closed

end of suitable thickness, as shown in *F*. This end is then heated and carefully blown to the smooth round end of uniformly thick glass, as shown in *G*.

**End-to-End Seals.** The simplest type of end-to-end seal occurs between tubes of equal diameter. The ends to be sealed together are first heated to red heat. There results a slight thickening due to the characteristic shrinking of the glass caused by

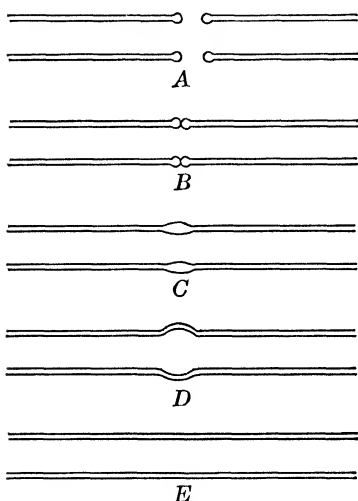


FIG. 5. Joining ends of equal size.

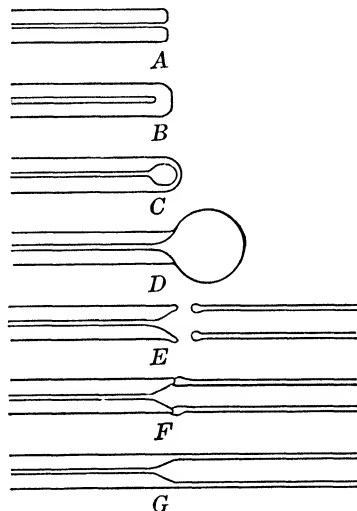


FIG. 6. Joining capillary to ordinary tubing.

surface tension as it becomes fluid (Figure 5, *A*). Then the ends are placed very gently together. A smooth seal depends on getting these ends together exactly. If at first touch they are not exactly aligned, it is better to remove the glass from the flame at once and break the two pieces apart as soon as they are cool enough, and try again. Otherwise much extra manipulation and blowing will be required to produce a smooth seal. It is a general principle of all glass blowing that, for best possible results with minimum effort, a correct start is essential.

When the ends are properly in contact, as in *B*, they may be forced together with slight pressure to insure a perfect closure. The two pieces are then handled as nearly as possible as if they

were one. They are rotated in the flame until the glass is quite fluid, as in *C*. The glass is then removed from the flame and promptly blown out to produce walls of uniform thickness, as in *D*. Immediately thereafter, while the glass is still soft, the ends are pulled apart until the bulge is removed, as in *E*. If the joint is not satisfactorily smooth, it may be reheated, shrunk, blown, and stretched as before, until it has the desired appearance.

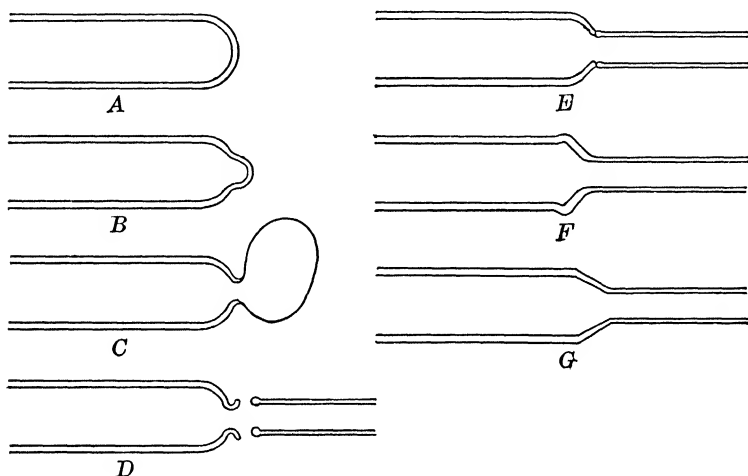


FIG. 7. Joining ends of unequal sizes.

In sealing ordinary tubing to capillary tubing, the capillary should first be prepared as shown in Figure 6. The end is closed by melting, and then blown into a small bulb as shown in *B* and *C*. Next, only the very end of this bulb is melted and blown out to a very thin bulb, as in *D*, which is broken off to leave an open end of flared bore as shown in *E*. This end is then sealed to the ordinary tubing exactly in the manner described above for sealing like tubes together.

The easiest way to seal pieces of capillary tubing together is first to prepare each end to be sealed as described for the capillary above.

The greatest difficulty in making smooth end-to-end seals is found in sealing tubing of unlike diameters together, because it is difficult to rotate such tubes simultaneously at equal angular



velocity while preserving the correct alignment. One method is to make a closed end in the larger tubing, and then heat the very center of the closed end with a small hot flame, blowing out a small bulge as shown in *B* of Figure 7. The end of this bulge is then heated, and a large, very thin bubble is blown out and broken off, leaving a hole of the same diameter as the bore of the smaller tube. The seal is made as in *E*, and the tapered section is heated strongly and uniformly, and then blown out

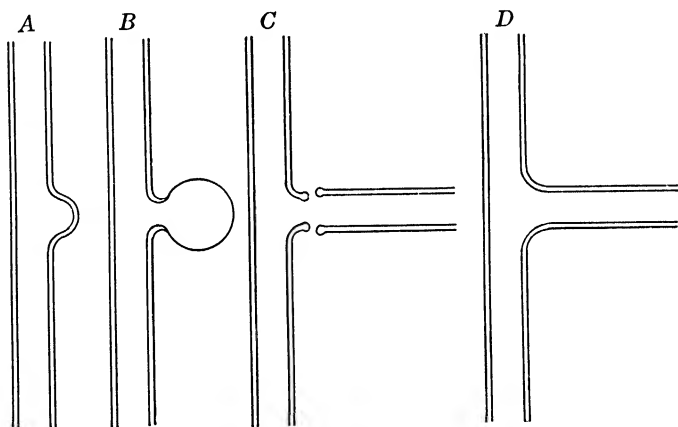


FIG. 8. Making a T-seal.

slightly and pulled out carefully to a smooth taper as shown in *G*. If the heated joint gets off-center, as it is very likely to do unless coordination of the two hands is very good, it may be brought back in line by thoroughly heating it until it is quite fluid, and then pulling it out and pushing it in slightly several times while realigning it.

**T-Seals.** These seals are made by heating a small area on one side of the tubing at the desired spot and blowing out a small bulge, as in *A* of Figure 8. If this bulge is then strongly heated until it shrinks back flat with the tubing, and reblown, several times, a rim or lip which is quite thick may be built up. Then the very end of the bulge may be strongly heated and blown out to a very thin bubble which can be broken off, leaving a short rim (*B* and *C*). The other tube is then sealed to this rim, smoothing the T-seal, as in *D*, by rotating the joint in the flame to heat

the whole area uniformly, and blowing out the lumps and unevenness. This uniform heating is difficult to accomplish without distorting the whole joint, and it is quite satisfactory to heat and blow smooth just one side or corner of the seal at a time.

**Ring Seals.** There are various methods of making ring seals. One of these is illustrated in Figure 9. First, a tube is inserted through a cork until the end almost touches the inside of a closed end of the large tube, as shown in *A*. The end of this large tube is then heated in the center until it shrinks back and fuses to

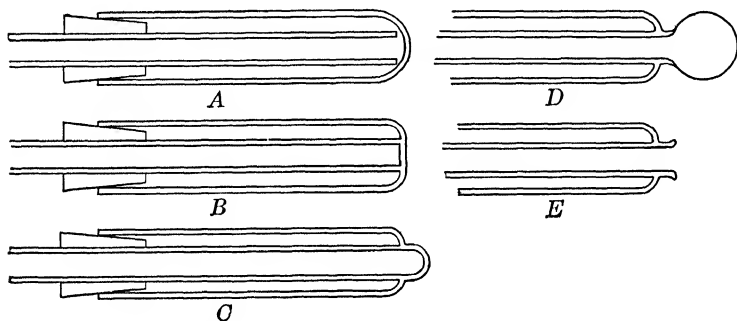


FIG. 9. Making a ring seal. Method I.

the end of the small tube, as in *B*. This spot is then heated and blown out, first to a thick-walled bulge as in *C*, and then the end of the bulge is blown to a thin-walled bubble, as in *D*, which is broken off to leave a rim as in *E*. Another piece of the smaller tubing is then sealed to this rim in the manner used to seal two equal diameter tubes together.

Another method is shown in Figure 10. First, a hole of the proper size is made, as previously described, in the rounded closed end of the larger tube. The smaller tube is heated separately at the point to be joined in the ring seal, and blown out slightly to make a larger diameter, just too large to fit through the hole in the larger tube. The two tubes are then held together as in *A* and *B*, and the seal is completed by fusing the glass together at the junction and blowing out for smoothness.

**Bends and Seals in Place.** Assembling and operating the high vacuum line require glass blowing in place. For the most part, this is restricted to the relatively simple operations of bending

and making end-to-end seals and T-seals. The essential difference between glass working in place and in the hands is that, in the former, the glass is not rotated in the flame; the flame is rotated about the glass. This operation requires a different kind of dexterity, but it is not difficult to learn.

The bending procedure is very similar to that described above except when the direction is down. Then gravity can be of assistance in helping to make a smooth bend, which can be made little by little. The operation is controlled slightly by the hand but mostly by the manner of heating.

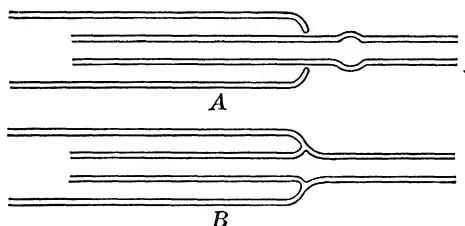


FIG. 10. Making a ring seal. Method II.

All in-place seals requiring the glass to be heated until it is fairly fluid are subject to the difficulty of having the hot glass flow downward. In general, therefore, it is best to minimize the time of heating, and also to work the glass at as low a temperature as possible. Ordinarily this gravitational flow of glass will not cause serious trouble, but, when a seal requires considerable reworking, it may in the process become very thin at the upper portion and undesirably thick at the lower part. This can be remedied, with care, if the lower section is not clamped or otherwise held in place, by heating the seal and pushing the lower section upward and pulling it down a little, several times. If the lower section cannot be moved, it may be necessary to reinforce the thin section by melting glass rod into the tubing at the uppermost part of the thin section, helping this extra glass to work down to thicken the weak parts by repeated heating and blowing. Points of unequal thickness are undesirable, even when well annealed, as thermal strains will be set up on subsequent heating because the thick spots will become heated more slowly and cool more slowly. Thick accumulations of glass which cannot be

worked back to their origin should therefore be removed. This can be done by melting the spot, pushing a piece of cold glass rod into the center, and pulling the excess glass out with it.

When blowing is done through an intricate system of tubes, and especially when there are some tubes of large volume, pressure control becomes much less delicate. There is a delay between applying pressure at the source and increasing pressure at the heated joint, and, similarly, the pressure at the joint continues for a little while after application at the source has stopped. Furthermore, when there are large volume and narrow tubes, one must blow considerably harder to produce the same effect. It is therefore necessary to learn to compensate for these variations when working the glass of a complex vacuum line, and it is preferable to attach a blowing tube as close as possible to the joint to be worked.

**Closed Circuits.** The problem of making closed circuits of glass tubing is essentially that of connecting two open ends which are in fixed position at some distance from each other. This operation involves sealing in place a piece of tubing which is of exactly the right length, or which can be made to fit by bending. Since normally both ends are not sealed simultaneously, the final problem is to fit the end of this piece of tubing to the desired opening and to seal it there.

Sometimes it is possible to measure and cut exactly the correct length of tubing, in which case making the closed circuit is fairly simple. More often, it is not possible to measure exactly. Then it seems better to take a piece which is somewhat too long, seal it in place at one end, bend it around to the second opening, and then cut it to the correct length. It may then be bent to fit closely, but it still may not be possible to push the two halves of the seal together when they are heated. Heating causes the glass to shrink back, and the fit is worse than before. Then a piece of Pyrex rod about 1 mm in diameter becomes very useful. The two ends to be sealed are heated strongly, and the glass rod is then thrust into the soft edge of one end and quickly pulled over to the other end. After cooling a moment, the rod can easily be broken loose and the process repeated. In this manner, the joint can be pulled together bit by bit. If this method involves stretching of the glass to the point of excessive thinning,

some of the glass from the rod may be incorporated in the joint at the desired places. Once the joint is thus closed so that it is airtight, it can be melted down and smoothed by blowing. By this method it is possible successfully to close a gap equal to the diameter of the tubing.

When such a joint is heated before it is completely sealed, shrinkage of the glass causes the narrow, unsealed cracks to become disconcertingly large, round holes. These may be filled with glass from a piece of rod, but it is much more satisfactory to pull them closed again by the procedure described above. Since all the original glass is still there, making up the rim of the hole, it is possible to close the hole completely without adding any new glass and without thinning the area.

Very small unsealed places, and cracks and holes in general, may often be sealed by applying heat carefully at one side of them and very gradually moving it nearer, until the molten glass fuses over the hole. If heat is applied directly at the unsealed spot first, however, it will almost invariably result in the glass spreading apart instead of melting together.

**Sealing off Apparatus in Vacuo.** In various procedures to be described later, which involve the removal of materials from the vacuum line without admitting air, it is necessary to seal off apparatus in vacuo. Two chief factors are involved. One is that glass which is evacuated, being under a pressure differential of 1 atmosphere, will collapse readily under this pressure when warmed to its softening point, and may even form a hole by "sucking in" if heated too hot. The other is that, no matter how thoroughly glass has been baked and evacuated, it will give off small amounts of gases such as water vapor, carbon dioxide and air, when heated to the necessary fluidity. The problem therefore involves making a smooth, strong seal under adverse circumstances and avoiding contamination of the contents of a tube by gases and vapors desorbed during its sealing.

If the eventual need for sealing off can be predicted, it is better to prepare in advance by forming a short, constricted section with thickened walls at the point to be sealed. When it is time for the actual melting down and pulling away of the tube, there will be less danger of part of the seal becoming overheated and blowing in to form a weak, thin spot. Only the thick-walled

section is heated, heat being applied very gradually and very uniformly until the walls begin to collapse under the pressure of the atmosphere. Slight tension is applied to elongate the softened section, and pumping is continued while the hollow part of the section becomes smaller and smaller. This procedure removes most of any desorbed gases until the very last moment, when the opening is quickly sealed shut, and the glass on the vacuum line side is then heated enough to permit pulling the whole tube entirely away from the line. The surplus thick glass at the end of the tube may then be removed by careful heating with a tiny flame and pulling away, avoiding heating the walls of the tube. Finally, the tip is annealed; annealing is particularly important if the tube is to be subjected to considerable pressure.

When it is necessary to seal off a tube or section of apparatus without the benefit of preliminary constricting and wall thickening, essentially the same procedure is followed, but much greater care is necessary to control the collapsing of the walls before the seal is completed. After the walls have collapsed almost to the point of closing the tube, all further heating should be applied on the side of the constriction away from the tube, while the tube is being pulled gently away from the heated area.

**Clamping Interconnected Apparatus.** The best way to clamp and support interconnected glass apparatus like that in a high vacuum line is not necessarily obvious. It is surprisingly difficult to place several clamps in positions to support intricate apparatus securely without placing on the apparatus considerable strain due to imperfect alignment.

Metal clamps should be padded for holding glass firmly, but not with resilient materials like rubber. Asbestos, in either sheet or powder form, is practically ideal. It is moistened and placed between the clamp jaws and the glass, and the clamp, aligned as carefully as possible, is closed snugly. When the asbestos has dried, it provides an adequately firm but not too rigid support for the glass, and it can be removed easily when necessary either by breaking away or by wetting and removing. Furthermore, it can be heated with a direct flame without being damaged.

When two or more clamps are placed firmly about the same piece of apparatus, it is very desirable to remove any possible

strain due to imperfect alignment by heating a section of the interconnecting tubing until it is soft enough to bend under the stress. This is the only way to be sure that the clamps are not exerting a stress on the glass.

Clamps should never be placed over or very near seals, where they may prevent the discovery of leaks in the most probable location by interfering with the functioning of the leak detector, as will be explained in the next chapter. They should, however, be placed as close as possible to all parts of the apparatus where stress is most likely to be applied, as, for example, near stopcocks.

There are a number of useful references for those who may wish to study the art and science of glass blowing in further detail.<sup>1</sup>

<sup>1</sup> For example, see R. H. Wright, *Manual of Laboratory Glass-Blowing*, Chemical Publishing Company, Inc., Brooklyn, N. Y., 1943; J. Strong, *Procedures in Experimental Physics*, Prentice-Hall, Inc., New York, 1944; J. D. Heldman, *Techniques of Glass Manipulation in Scientific Research*, Prentice-Hall, Inc., New York, 1946; W. E. Barr and V. J. Anhorn, "Scientific Glass Blowing and Laboratory Techniques," published as a serial in *Instruments*, beginning 18, 874 (1945), and continuing monthly into 1947.

## *Producing a High Vacuum*

### GENERAL PRINCIPLES

As previously mentioned, the technique of handling volatile materials in a high vacuum system depends upon the fact that gases diffuse rapidly throughout a vacuum. This makes it possible to transfer volatile materials to any desired part of the system merely by cooling that part to a temperature at which the materials have a very low vapor pressure. There they continue to collect and condense until only that concentration of vapor is left throughout the system which is in equilibrium with the condensed phase at the low temperature.

In the absence of appreciable amounts of noncondensable gases, this transfer of volatile materials to a cooled zone takes place rapidly. However, in the presence of even small concentrations of noncondensable gases, the diffusion of the condensable vapors is much slower, simply because the noncondensable molecules get in the way. It is necessary to keep the partial pressure of noncondensable gases below  $10^{-3}$  mm of mercury, and preferably below  $10^{-4}$  mm, in order to effect quantitative transfers of condensable materials at a practical rate. The removal of noncondensable gas from the system must therefore be accomplished before condensable materials can be efficiently handled. This calls for a good pumping system, capable of producing the necessary high vacuum in a reasonably short time.

For the present purposes, it is not necessary to consider in detail the theory and practical measurement of pumping speeds at low gas pressures. This subject is adequately treated in most books dealing with the production of high vacua from the standpoint of the physicist. However, before the required pumps are considered, it should be useful to create a mental picture of the



molecular activity within an enclosed space which is being evacuated.

Each gas molecule in the enclosed vacuum apparatus is traveling rapidly (at a rate of the order of 1000 feet or more per second) in a straight line in a random direction; it strikes another molecule and bounces away in another direction with perfect elasticity. At atmospheric pressure and 25°C, there are  $3.26 \times 10^{16}$  molecules per milliliter, all traveling in random directions and at the same average high speed. Since these molecules are of appreciable size (oxygen and nitrogen molecules are approximately 3 Å in diameter), there are innumerable collisions. The average distance which a molecule travels between collisions is called the "mean free path," which may be calculated by use of the equation

$$\lambda = \frac{1}{\sqrt{2} \pi n d^2} \quad (1)$$

where  $\lambda$  is the mean free path in centimeters,  $n$  is the number of molecules per milliliter, and  $d$  is the molecular diameter in centimeters. At 25°C, this equation can be shown to take the form

$$\lambda = \frac{0.069}{P d^2} \quad (1a)$$

where  $\lambda$  is the mean free path in centimeters,  $P$  is the pressure in millimeters of mercury, and  $d$  is the molecular diameter in Angstrom units ( $10^{-8}$  cm). Thus at atmospheric pressure and 25°C, air molecules travel an average of only  $10^{-5}$  cm between collisions.

With this concept of molecular activity in mind, consider the behavior of a gas introduced at one end of an evacuated space. There is no attractive force compelling any individual molecule of that gas to travel to the other end. However, it is obvious that any rapidly moving, perfectly elastic particle such as the ideal gas molecule will tend eventually to move toward the other end because it will encounter less resistance (have fewer collisions) in that direction. In other words, the mean free path in the direction of the other end is longer than in any other direction, and therefore there is a net movement, or flow, of gas toward

that end. The result of this kinetic, molecular nature of a gas is that it diffuses most readily through a vacuum, or in any direction where the mean free path is longer. The motive power for gas flow is inherent in the gas; it cannot result from a mechanical force applied at a distance.

It is apparent from this molecular picture that a pump can have no actual attraction for the gas. The best possible pump can do no more than remove permanently those molecules which wander into it. The only reason why there is any net movement of molecules in the system toward the pump is that, when some of the molecules diffuse into the pump and are removed, the adjacent molecules can then travel farther, on the average, toward the pump than in other directions, before colliding. This is an adequate reason for gas flow, and, in practice, evacuation of the bulk of the air from an enclosed system is effected rapidly with a reasonably good pump.

Removal of the last part of the air, however, presents much greater difficulty. The air molecules are, of course, colliding not only with each other but also with the walls of their container. At all but very low pressures, the mean free path is so short compared to the dimensions of the container that these collisions with the container can have only a negligible effect on the flow of gas toward the pump, since they are far outnumbered by intermolecular collisions. However, as the concentration of molecules becomes smaller, the mean free path becomes longer, as seen from equation (1). At  $10^{-2}$  mm it is equal to 0.77 cm, which is beginning to approach the dimensions of the container, and at  $10^{-4}$  mm it is 77 cm. At these low pressures, therefore, the number of collisions with the container walls approaches and exceeds the number of intermolecular collisions. It has been found experimentally that this change in the average type of collision has a significant effect on the rate of diffusion of gas toward a vacuum pump. When the pressure has been reduced to a point where the mean free path of the molecules is relatively large in comparison with the dimensions of the container or tube, the resistance of the tube to gas flow becomes proportional to the length and inversely proportional to the cube of the radius.<sup>1</sup> It is

<sup>1</sup> M. Knudsen, *Ann. Physik*, **28**, 75, 999 (1908); W. Gaede, *Ann. Physik*, **46**, 357 (1915); I. Langmuir, *Phys. Rev.*, **8**, 48 (1916).

interesting to speculate that this may be due in part to micro-irregularities of the surface of the inner walls and in part to inelasticity of the collisions with the walls, or sorption. A theoretical treatment is beyond the scope of this discussion, however. The important point is that the rate of diffusion of gas toward a pump at low pressures is very much affected by the dimensions of the tube.

It can be seen from the above discussion that there are two equally important factors to be considered in providing for the rapid removal of noncondensable gases from a vacuum system. Pumps must be used which are capable of efficient elimination of all gas molecules reaching them down to a very low pressure, and also it must be possible for gas molecules to reach them by as rapid diffusion as possible.

Modern pumps are very efficient. On the other hand, it is not practical to avoid small dimensions in parts of a general purpose chemical high vacuum line. Therefore the fact must be recognized that the dimensions of the line, not the pumps, limit the speed at which noncondensable gas can be ejected. No advantage is to be derived from using better pumps than are justified by the dimensions of the system to be evacuated. The general principle of keeping all connecting lines large in diameter where practical, however, should be observed. With main lines about 20 mm in diameter, connecting lines 8 mm in diameter, mercury float valves, and one or two stopcocks of not less than 3–4 mm bore, an average high vacuum system, properly conditioned, can usually be pumped from a pressure of 1 atmosphere of dry air to below  $10^{-4}$  mm in 20–30 minutes, with a pumping system like that described below.

## VACUUM PUMPS

Two pumps are needed, to operate in series. One is a diffusion, or “condensation” pump, capable of producing the high vacuum needed, and the other is a mechanical pump, which produces a rough vacuum necessary for proper operation of the diffusion pump.

**Diffusion Pumps.** These are devices wherein gas molecules diffusing from a system to be evacuated are irreversibly entrained

by a stream of vapor which sweeps them to where they can diffuse into a second pump capable of ejecting them into the atmosphere. The vapor is condensed and returned to a boiler, where it is re-evaporated and recycled continuously past the point of entrainment. The most useful type of diffusion pump, often referred to as a "condensation pump" because it provides for prompt condensation of the vapor shortly after the vapor has passed the point of entrainment, was invented by Langmuir.<sup>2</sup> Innumerable variations of the basic design have been proposed, mostly with the objective of increasing pumping speeds, but one of the simpler modifications will be found quite satisfactory for use with the type of high vacuum system to be described herein. For example, a practical design with suitable dimensions is shown in Figure 11. A pump of this type can be constructed by a competent glass blower without great difficulty.

The original diffusion pumps used mercury as the liquid for distillation; recently, high boiling organic oils have frequently been used instead. Some of the oil-filled pumps are said to be more rapid in action, but, owing to the comparative susceptibility of oils to oxidation and contamination, mercury diffusion pumps seem preferable for chemical high vacuum work.

The mercury pump illustrated functions as follows. It is installed between the vacuum system at *B* and a mechanical fore pump at *C*. The fore pump, which will be described below, evacuates the system including the mercury pump to a pressure below 1 mm and preferably below 0.1 mm. The mercury in the boiler is then heated to boiling. (The boiler illustrated, which permits heating by means of an inset electric heating unit such as can be purchased to screw into an ordinary electric lamp socket, is very satisfactory in providing for smooth ebullition of the mercury. In view of the fragility of glass and the density of mercury, this is a desirable attribute, as superheating with consequent "bumping" is to be avoided.) The vapors of mercury stream out of the opening at *A*, there entraining air molecules which diffuse there from *B*. Within a short distance, the mercury vapor strikes the cooled walls and condenses, to return to the boiler via the return trap. The entrained air is thus liberated

<sup>2</sup> I. Langmuir, *Gen. Elec. Rev.*, **19**, 1060 (1916); *J. Franklin Inst.*, **182**, 179 (1916).

in the condenser tube and is accumulated there until it diffuses out at the pressure resulting from the fore pump. There is thus

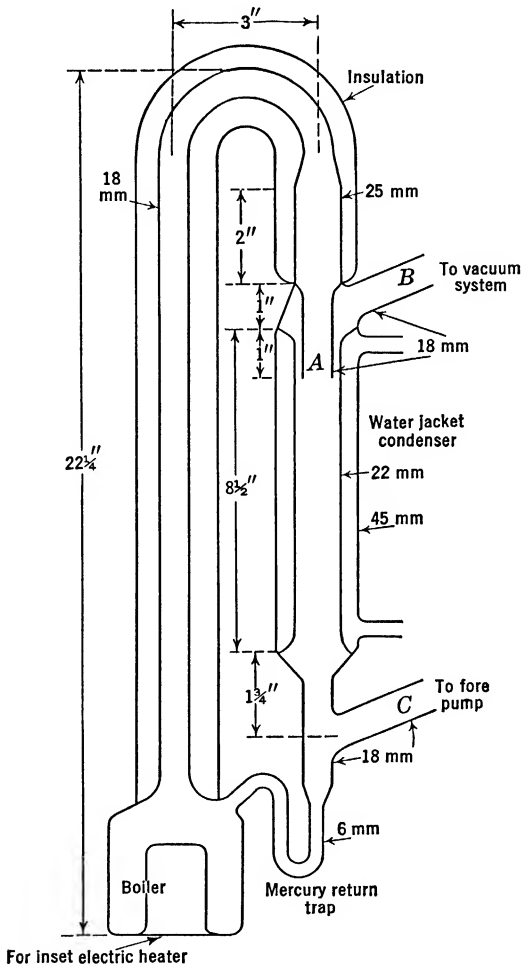
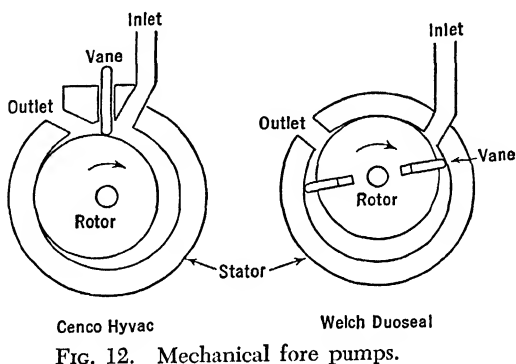


FIG. 11. Mercury condensation pump. All tubing dimensions O.D.  
(Courtesy of C. J. Lewis.)

maintained a pressure differential between the air in the condenser tube and the air in the vacuum system, but it cannot be equalized because the air cannot effectively diffuse back into *B* against the steady stream of mercury vapor. Backed by an ade-

quate fore pump, such a diffusion pump is easily capable of producing a vacuum in a good system better than  $10^{-5}$  mm.

**Mechanical Fore Pumps.** There are two common makes of mechanical fore pumps on the market, both of which are suitable for backing a mercury diffusion pump of the type described. One is the Cenco Hyvac, sold by the Central Scientific Company, and the other is the Welch Duoseal, a product of the Welch Scientific Company. Both work on the principle of continuously and irreversibly sweeping gas from an inlet to an outlet, under protec-



tion of an oil seal. In detail they are somewhat different, the essential differences being illustrated in Figure 12. The Hyvac pump has inlet and outlet ports close together, separated by a single vane which passes through the casing and is constantly held against a cylinder by means of a spring. The cylinder rotates eccentrically about an axis which coincides with the center of the casing. The Duoseal pump, on the other hand, has ports farther apart, separated only by an oil seal of  $1/10,000$ -inch clearance between a cylinder which rotates on center and the stationary part or stator. Here the air is not swept out by the cylinder itself, as in the Hyvac, but by vanes, mounted in the cylinder, which are held constantly against the stator inner wall by springs.

The Welch pump operates at a somewhat higher oil bath temperature. This has the advantage of slightly more rapid removal of volatile contaminants by evaporation, and the disadvantage of making the oil slightly more susceptible to deterioration by oxida-

tion. The Welch pump operating at high vacuum is practically silent, but the Hyvac pump is not. Both pumps should be protected against corrosive vapors; it is believed that the Welch pump may be somewhat more susceptible to operating failure from such vapors, because of corrosion at the close clearance seal between rotor and stator.

Both types of pumps are provided with means of preventing the oil from being forced back into the inlet port when the pump

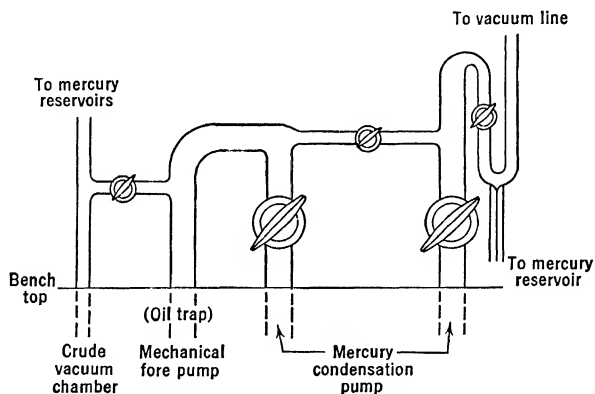


FIG. 13. Suggested system for connecting pumps to vacuum line.

is left shut down while attached to an evacuated system. However, it is very much easier to install, between mercury pump and fore pump, a trap capable of containing such oil if the means of restraining it should fail than it is to disconnect and clean and refill a mercury diffusion pump which has become flooded with oil.

**Pump Connections.** Figure 13 suggests a method of connecting the vacuum pumps to the system. It is desirable to provide a bypass for the diffusion pump so that the mechanical fore pump may be used directly to evacuate the system. When operations with the vacuum system require temporary admission of air followed by its removal, it is better to remove the bulk of it without passing it through the hot diffusion pump, where it accelerates the formation of mercury oxide scum and from which it may sweep appreciable quantities of mercury vapor over into the fore pump. Although experience has shown that the amount

of mercury which may collect in the fore pump with normally careful use is not harmful, there is no point in needlessly contaminating the fore pump with mercury.

Numerous mercury reservoirs will be described in later sections as parts of the high vacuum apparatus. These need a rough vacuum source for operation. Although a water aspirator can provide the necessary vacuum, it has been found very convenient to have a separate vacuum chamber which can be evacuated intermittently by the fore pump, and which will operate the mercury reservoirs. The requirements and construction of such a chamber will be described in a later section; Figure 13 shows how it can be connected.

From the high vacuum apparatus via the diffusion pump to the fore pump, a continuous glass line is best. Here the glass must be joined in a vacuum-tight seal to the metal inlet of the fore pump. This can be done satisfactorily by bringing the glass end very close to the metal tube opening and joining the two by means of a coupling of thick rubber tubing. The coupling may be held securely by ordinary metal hose clamps and lacquered at the ends.

**Location of Pumps.** The diffusion pump and the fore pump, as well as the vacuum chamber, should be easily accessible but out of the way, since once assembled, they rarely need attention. It has been found convenient to mount them in an enclosing cabinet beneath the bench top supporting the high vacuum apparatus, with only the stopcocks above the bench top. This arrangement has an added advantage in minimizing the possible hazard due to contamination of the room atmosphere by mercury vapor from the diffusion pump. No matter where the pumps may be located, however, it is good practice to provide for efficient ventilation, as by a funnel inverted over the mechanical pump air outlet and connected by rubber tubing to a laboratory vacuum source or a small air pump under a hood.

## EVACUATING THE APPARATUS

A leak-proof high vacuum apparatus connected to an adequate pumping system is necessary but not sufficient for the production of high vacuum. It is a simple matter to remove all the air down



to a pressure below 1 mm, but, from there on down, mere application of the pumps would prove very discouraging, especially when the glass has been newly exposed to ordinary atmospheric air and moisture. The reason for this is that glass holds tenaciously on to appreciable amounts of carbon dioxide, air, and moisture by sorption, and these are released in vacuo only extremely slowly at ordinary temperatures. In fact, it is necessary to heat the glass to about 300°C in order to liberate the adsorbed gases at a rapid rate, and, at higher temperatures, gases from beneath the surface of the glass are given off indefinitely. In order to obtain as high a vacuum as desired, therefore, it is necessary to "bake out" the new apparatus by heating it, while pumping, with a gas-air "brush" type of flame. A rough qualitative indication of temperature is the color of the flame while the glass is being heated. As the glass approaches the point at which it is sufficiently soft to collapse under pressure of the atmosphere, it begins to impart a pink color to the gas flame which would soon turn to the familiar blinding yellow sodium flame if the heat were continued. In order to prevent distortion or collapse of the glass, heat should be removed as soon as the pink color occurs. Repeated heating of the apparatus is necessary in order to drive away enough of the sorbed gases so that a good vacuum may thereafter readily be obtained.

When the apparatus is new, it will be found to give forth gases very slowly at room temperature, even after baking. After it has been kept evacuated for some time, however, with intermittent heating, it gradually becomes conditioned, and it may be evacuated more quickly and will hold its vacuum better. Even so, it is usually desirable to rebake it after every exposure to vapors, particularly those of relatively high boiling liquids or of polar substances, such as water, ammonia, and hydrogen chloride, which are strongly sorbed by the glass.

## LOCATING LEAKS

The best of glass blowers sometimes leave tiny holes in what appear to be perfect seals. Ordinary amateur glass blowers frequently do. Presumably these usually are not due to failure to force the members firmly enough together in making the seal, or

to failure to melt the glass down enough to provide material continuity at the seal, but to such causes as minute specks of dirt which prevent perfect fusion of the glass.

In addition to these tiny holes, sometimes microscopic cracks, due probably to imperfect annealing, appear in the glass.

Besides these imperfections which may occur as an immediate result of the fabrication of the apparatus, there are sometimes weaknesses where holes not initially present develop on standing.

A vacuum of the desired degree cannot be produced or maintained if leaks are present. Fortunately, there is an excellent tool for locating very small holes—the high frequency spark discharge coil known as the Tesla coil. This instrument discharges a stream of sparks in all directions into the air. Wherever there is a stream of air flowing into a hole in the apparatus, these sparks converge into a single beam which goes directly to the hole, so that its exact location can readily be seen. The Tesla coil is extremely useful for finding leaks in glassware under vacuum (below 1 mm), except, of course, within a half inch or so of iron clamps, which will attract the spark more strongly than the hole. The chance of a leak occurring along an unworked length of tubing is very remote compared to the chance of a leak at a seal; consequently, if clamps are kept away from seals, the Tesla coil is capable of finding virtually all leaks which may occur in the apparatus, except sometimes in lubricated glass joints, as discussed below.

Some workers advise caution in the use of the Tesla coil, pointing out that a strong spark is capable of forming holes where none existed previously. However, it is far better to locate and eliminate all weaknesses and potential sources of leaks than to have leaks occur during an experiment.

Leaks in glass may be temporarily closed by application of a small amount of a wax such as picein. For permanent repair, it is sometimes possible to fuse the glass together at the hole merely by melting and blowing, but a surer method is to remove some of the glass at the imperfection first, replacing it if necessary with fresh glass from a thin Pyrex rod. By this means, the impurity causing the initial imperfection or failure will be removed.

Whenever stopcocks or other lubricated ground joints are part of the system to be evacuated, they should be under constant suspicion as possible sources of leaks. Such leaks are not easily detected by the Tesla coil, but they may usually be discovered by visual inspection of the ground joint. If the lubricant forms a perfectly clear, transparent film over the entire ground area, leakage is very unlikely. If the film shows minute areas or streaks of opaqueness, or any sign whatever of channeling, the joint may or may not be leaking, but it should be relubricated or the lubricant should be worked in better as a precaution. Visual inspection is not infallible, however. When all search for leaks fails, cleaning and carefully relubricating all ground joints in the system will usually result in elimination of leakage.

It is always well to bear in mind that the slow desorption of gases from the inner walls of the system or from contaminated ground joint lubricant may be mistaken for leakage. Even an enclosed system entirely without leaks cannot be expected to maintain a high vacuum for any extensive period of time unless most of such sorbed gas has first been removed.

## NATURE OF THE VACUUM PRODUCED

It should be remembered that in references to vacua better than  $10^{-3}$  mm herein, the presence of mercury vapor is being ignored. Actually, since the high vacuum apparatus contains mercury, mercury vapor at a pressure of about  $2 \times 10^{-3}$  mm will be present. Since this vapor is chemically quite inert and is readily condensable, it does not interfere seriously with evaporation-condensation processes within the system. This presence of mercury vapor is an important difference between high vacua, as used in the experimental methods of chemistry described herein, and high vacua in physics, where the necessity for a closer approach to absolute vacuum makes the trapping out of mercury vapor imperative. Incidentally, it also accounts in part for the growing preference for oils as pump liquids, whose vapor pressure is very much lower than that of mercury. As stated earlier, mercury still seems to be the best diffusion pump liquid for general chemical work.

To maintain a proper perspective in the concept of high vacuum, it is well to realize that, even if the presence of mercury vapor is disregarded, the best vacuum normally produced in chemical high vacuum apparatus is  $10^{-6}$  mm. Although this reduces the concentration of air molecules to a point at which they do not interfere appreciably with the diffusion of other gases and vapors in the system, there are still over thirty-five thousand million air molecules per milliliter.

## *Measuring Pressure*

### LOW PRESSURE

There are a number of gages<sup>1</sup> which are capable of measuring the low pressures attainable in the chemical high vacuum system, but for the general purposes to be described herein there is none more suitable than the McLeod gage.<sup>2</sup> This is a device based on Boyle's Law, which states that the product of the volume and the pressure of a gas is a constant. The gage provides a means of cutting off a definite large volume of gas which is at the low pressure to be measured, and compressing it into so small a volume that the pressure becomes high enough to be measured by an ordinary mercury manometer. If the large known volume is  $V$  and the pressure is  $P$ , and if the gas is compressed to a measured small volume  $v$  at a pressure  $p$  which can be measured directly, the low pressure  $P = pv/V$ .

Many modifications of the McLeod gage have been suggested. The simple design shown in Figure 14 is quite satisfactory. The mercury reservoir may be constructed from a 200-ml round-bottom flask, and the bulb from a 50-ml flask. A capillary with a bore 1 mm in diameter is suitable, provided the bore is uniform. The uniformity may be determined by measuring the length of a thread of mercury at various positions along the capillary. The diameter may easily be calculated from the length of the mercury thread, the density of the mercury at the temperature of measurement, and the weight of the mercury. The capillaries  $B$  and  $B'$  should be constructed from the same uniform piece. The bulb and capillary section may be calibrated with sufficient accuracy

<sup>1</sup> For a description and discussion of these, see M. F. Behar, *Instruments*, **4**, 231-242 (1931); S. Dushman, *Instruments*, **20**, 234-239 (1947).

<sup>2</sup> McLeod, *Phil. Mag.*, **47**, 110 (1874).

by measuring the volume of liquid necessary to fill it before sealing it to the rest of the gage at *A*.

To operate the gage, its upper part is opened to the system whose pressure is to be measured by drawing the mercury down

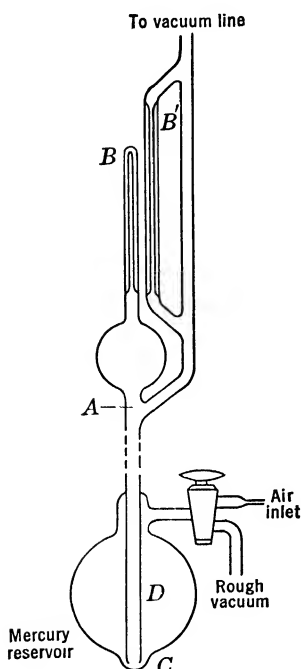


FIG. 14. McLeod gage.

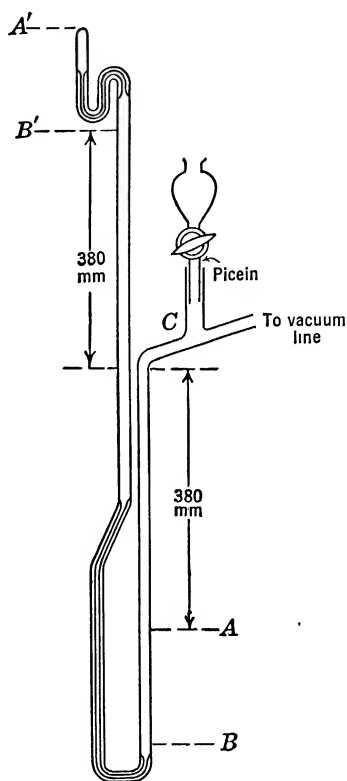


FIG. 15. Manometer and method of filling.

well below *A* by means of a rough vacuum exerted on the reservoir. Then air is carefully admitted to the reservoir, forcing the mercury up past *A* and thus compressing the gas above that point into the capillary. The gage is usually read with the mercury level in capillary *B'* exactly opposite the top of capillary *B*. It is generally necessary to tap the capillaries gently to adjust the mercury level to insure that the mercury does not stick at the

wrong place. The pressure to be measured is then equal to the product of the gas volume in capillary *B* times the pressure as measured by the difference in mercury levels in capillaries *B* and *B'*, divided by the volume of the gage above *A*.

Unless the capillaries are perfectly clean, the gage may not register accurately because of sticking of the mercury. Therefore it is especially important to use pure mercury and to avoid contamination. The capillaries may be freed of mercury oxide scum and other surface impurities by thorough evacuation at a temperature just below the softening point of the glass. Furthermore, the gage will not measure accurately the pressure due to easily condensable vapors, since these may actually be partially liquefied in the capillary when they are compressed.

A McLeod gage may be broken, if air is admitted too rapidly to the reservoir, by the quick surge and impact of mercury in the bulb. A capillary air inlet is therefore provided, and the mercury tube *D* extends into the pit at *C* to minimize the possibility of getting an air bubble into the mercury column. To be doubly safe, the bottom of the tube *D* could be constricted at *C* to a diameter of about 2 mm, but this would be at the expense of more rapid operation of the gage.

The mercury reservoir should be firmly supported by a cork ring or, better, by a form-fitting base of plaster or asbestos. Plaster of Paris is mixed with water to form a slightly fluid paste which is poured into a shallow wooden or heavy cardboard box a little larger than the reservoir bulb. The bulb is coated with oil, to prevent sticking to the plaster, and held in the plaster from one-third to halfway immersed for the few minutes necessary for the plaster to set.

A McLeod gage of the dimensions given above is by no means a precision instrument.<sup>3</sup> It would not be suitable for highly accurate measurements of pressures below  $10^{-3}$  mm, but it is adequate to give a semi-quantitative measure of whether the vacuum is sufficiently good, which is all that is ordinarily required in chemical high vacuum work.

<sup>3</sup> For an example of a more accurate gage, see P. Rosenberg, *Rev. Sci. Instruments*, **10**, 131-134 (1939). For a general discussion, see L. Dunoyer (trans. by J. H. Smith), *Vacuum Practice*, D. Van Nostrand Co., New York, 1926, pp. 61-74.

**ORDINARY PRESSURE**

A mercury manometer suitable for ordinary pressure measurement, ranging from a few tenths of a millimeter to about 1 atmosphere, is shown in Figure 15, together with a method of filling it. Such a manometer may be constructed from 2-mm capillary tubing and 10-mm tubing. It is necessary to seal a temporary side arm on at *C* to admit a dropping funnel for adding mercury. The dropping funnel is sealed into the side arm with picein.

The procedure for filling follows. The entire manometer is thoroughly baked under the highest vacuum attainable with the pumps. When this process is complete and the glass is cool, clean mercury is added from the dropping funnel, the vacuum being maintained, until the manometer is filled to the indicated mark. Dry, CO<sub>2</sub>-free air is then admitted to the vacuum system, the side arm is pulled away at *C*, and the glass is worked to provide a smooth, uninterrupted tube from the manometer to the vacuum system.

No matter how thoroughly the manometer is degassed before it is filled, there is likely to be a very slow evolution of sorbed gases from the glass into the space on the dead-end side of the manometer. The small trap at the top of the manometer is provided for the purpose of renewing this Toricellian vacuum when necessary. By use of compressed air, the mercury is forced up to the very top at *A'*. Then the air pressure is released to allow the mercury to fall back to its normal position at 1 atmosphere pressure. As it falls through the bent capillary, this is tapped sharply to break the mercury thread. A small thread of mercury thus remains in the capillary, retaining in the small bulb at the top of the manometer any gases carried up by the rising mercury column. Obviously it is important in constructing the manometer to allow ample space between *A* and *B* to supply mercury to fill the volume from *B'* to *A'*.

When the manometer is perfectly clean and of the above-mentioned dimensions, it should be accurate to within about 0.2 mm. In order to keep the manometer clean, it is advisable to bake out the pressure side after it has been exposed to vapors. This can be done crudely by cautiously warming the mercury



at a very low pressure and tapping the manometer intermittently to permit the bubbles of desorbed gas to rise through the mercury. A more thorough degassing can be accomplished if the mercury is out of the way. Dry air is admitted to the system to shift the mercury to the position corresponding to 1 atmosphere pressure. While it is in this position, a small piece of cotton saturated with liquid nitrogen is wrapped around the capillary at the bottom of the manometer and kept there, with nitrogen frequently replenished. This freezes a small plug of mercury in the capillary, which immobilizes the rest of the column. The air may now be evacuated, leaving the manometer still reading 1 atmosphere pressure, and the pressure side of the manometer may be baked out under vacuum. The mercury plug is kept frozen until the baking and outgassing is complete, and the glass has cooled, when it is allowed to melt again and the manometer is once more ready for use.

Table I gives corrections for the thermal expansion of mercury, since pressure is conventionally measured in millimeters of mercury at 0°C. At ordinary room temperature (about 25°C) the correction is negligible (less than 0.2 mm) for pressures under about 50 mm.

TABLE I. PRESSURE CORRECTION FACTORS FOR THERMAL EXPANSION OF MERCURY

(Factor times observed  $P$  = corrected  $P$ )

<i>Temperature,</i> °C	<i>Factor</i>	<i>Temperature,</i> °C	<i>Factor</i>
15	0.9973	26	0.9953
16	0.9971	27	0.9951
17	0.9969	28	0.9950
18	0.9968	29	0.9948
19	0.9966	30	0.9946
20	0.9964	31	0.9944
21	0.9962	32	0.9942
22	0.9960	33	0.9941
23	0.9959	34	0.9939
24	0.9957	35	0.9937
25	0.9955		

## *Low Temperatures*

### PRODUCING LOW TEMPERATURES

The basic materials for the production of low temperature baths for chemical high vacuum work are liquid nitrogen, solid carbon dioxide, and, to a lesser extent, liquid ammonia. These may be used to produce baths of any desired temperature between  $0^{\circ}\text{C}$  and  $-210^{\circ}\text{C}$ . A thorough understanding of the nature of these substances is very worth while.

**Liquid Nitrogen.** Of the refrigerants mentioned above, liquid nitrogen is the most indispensable and the most versatile, since it alone can be used to produce the entire low temperature range ordinarily needed. Liquid nitrogen is obtained through liquefaction of air. It is a clear, very mobile liquid, which maintains itself at its boiling point ( $-196^{\circ}\text{C}$ ) at atmospheric pressure by the cooling produced by evaporation. It may be used for producing lower temperatures down to about  $-210^{\circ}\text{C}$  by evaporating with a vacuum pump. It may be used directly as a cooling bath or, indirectly, to cool some other liquid bath medium.

Liquid nitrogen evaporates very rapidly unless it is efficiently shielded from sources of heat. It can only be stored with real economy in a highly evacuated, silvered Dewar flask, loosely stoppered. (Obviously it must never be tightly confined.) Large metal containers are commercially available which are less efficiently insulated but much more practical for obtaining and transporting liquid nitrogen from the producers, and for larger scale storage.

Liquid nitrogen should be handled with due regard for its ability to damage human tissues by freezing. The eyes in particular should be protected against the spattering which may occur, not only during pouring, but also as a result of extremely

rapid evaporation when the liquid comes in contact with a warmer material. In small amounts, however, liquid nitrogen is less hazardous than some other refrigerants, because it evaporates so rapidly when spilled on the skin that a gaseous cushion practically prevents actual contact of the liquid. This minimizes the damage, causing chiefly a tingling sensation.

Liquid nitrogen is a very rapidly acting coolant, not only because of its low temperature but also because of its mobility. Therefore, good practice is to introduce it into or around glass vessels with care, a little at a time, to lessen the risk of fracture due to thermal strain. Pyrex Dewar flasks are preferred containers, and even these are best cooled by rinsing with a small amount of liquid nitrogen first, before they are filled. Well-constructed vacuum flasks made of glass which is not Pyrex may be used to contain liquid nitrogen if preliminary cooling is carefully carried out by rinsing with successive small portions of the liquid; otherwise they are very apt to shatter. As for tubes of a vacuum apparatus, such as condensation traps, the chance of breakage due to thermal shock by sudden immersion in liquid nitrogen is extremely slight if the glass is thin-walled, properly annealed Pyrex. However, the fact that the chance exists is adequate reason for observing some degree of caution in cooling with this refrigerant.

The above discussion of the physical properties and use of liquid nitrogen might seem sufficient, in view of the fact that, from a chemical standpoint, pure liquid nitrogen is inert. However, because of its lower boiling point, it is capable of absorbing and condensing oxygen (b.  $-183^{\circ}\text{C}$ ) from the air, and it is possible for liquid nitrogen which has been exposed to the atmosphere for some time to contain an appreciable concentration of oxygen. It is also possible for liquid nitrogen as originally obtained from the source of production to contain some oxygen. Since mixtures containing liquid oxygen and combustible materials can be violently explosive, liquid nitrogen may be potentially hazardous, depending on its purity. It is difficult to know the extent or degree of this hazard, but it is important to recognize where such a hazard may exist.

Formerly liquid air (liquid nitrogen containing 20% oxygen) was used instead of liquid nitrogen, and it is sometimes still used,

for vacuum work. It was not uncommon practice to prepare cooling baths by mixing the liquid air directly with very inflammable materials like carbon disulfide. This was usually accomplished without accident, but now and then, without warning or apparent reason, there would be a violent explosion.<sup>1</sup> H. Staudinger<sup>2</sup> investigated this explosiveness and found that 1 ml of ether mixed with about 2 ml of liquid air, when ignited by a spark, exploded with the force of 4 g of nitroglycerin. Such mixtures did not necessarily require a spark, being also sensitive to friction and concussion. The severity of the explosion was diminished by dilution with nitrogen or in mixtures not of optimum concentration.

Obviously liquid nitrogen, even if impure, would be less hazardous than liquid air. Nevertheless, some hazard may exist wherever "liquid nitrogen" comes in contact, or might by accident come in contact, with combustible materials. Liquid nitrogen comes purposely in contact with combustible materials when it is used to cool such materials for low temperature baths by direct mixing. It could accidentally become mixed with such materials whenever it comes in contact with a glass tube containing them, either by breakage due to thermal shock or by actual mechanical force as in striking the tube against the edge or bottom of the Dewar flask. Although the risk may be considered relatively slight, safety goggles should be worn whenever such a hazard might exist. Where liquid air is used in place of liquid nitrogen, it is much wiser never to take the risk.

Such risks can be practically eliminated by using these coolants indirectly. When the liquid nitrogen is to be used for preparing a cooling bath, it can be placed in a metal container such as a large, thick-walled aluminum or copper test tube, which is immersed in the medium to be cooled.<sup>3</sup> With thorough stirring and, as necessary, occasional scraping of solid from the outside of the metal vessel, cooling of combustible material can be satisfactorily accomplished without hazard. A procedure<sup>4</sup>

<sup>1</sup> See, for example, W. Biltz, *Chem.-Ztg.*, **49**, 1001 (1925); A. Mittasch and E. Kuss, *Chem.-Ztg.*, **50**, 125 (1926).

<sup>2</sup> *Z. angew. Chem.*, **39**, 98 (1926).

<sup>3</sup> A. Stock, *Ber.*, **53**, 751 (1920).

<sup>4</sup> F. Henning and A. Stock, *Z. Physik*, **4**, 226 (1921).

for avoiding immersion of a tube in liquid air or nitrogen is to use a thick aluminum block with one hollow chamber to contain the tube to be cooled, and another hollow chamber to receive the liquid air at a controlled rate to produce the desired cooling. The entire block is suspended in a Dewar flask as a means of insulation.

**Solid Carbon Dioxide.** Solid carbon dioxide, commercially and familiarly known as "dry ice," is merely the solid form of carbon dioxide, which has a sublimation point at atmospheric pressure of  $-78.5^{\circ}\text{C}$ . It is purchased in solid cakes, which are easily broken into smaller chunks and reduced to a fine powder if they are wrapped in a stout cloth and shattered with a wooden mallet. Since it maintains its low temperature by evaporation, obviously it must never be tightly confined. Dry ice can cause injury if placed in contact with the skin. Solid pieces can be handled lightly with dry hands with relative impunity, but, if the skin is moist, the dry ice is apt to stick to it by the medium of a layer of water ice, causing real freezing before it can be removed. When dry ice is broken, the eyes should be protected from flying particles.

Dry ice may be used to produce any low temperature down to about  $-100^{\circ}\text{C}$ . Temperatures below  $-78.5^{\circ}\text{C}$  may be reached by pumping gas away from a dry ice-liquid medium mixture with a vacuum pump, even a water aspirator. The most frequent use of dry ice as a coolant, however, is for maintaining the carbon dioxide sublimation temperature of  $-78.5^{\circ}\text{C}$ , or temperatures in that vicinity. Finely pulverized dry solid may be used for this purpose, but it is usually preferable to provide better contact by means of a liquid medium. The liquid medium may be any material inert to carbon dioxide which is very fluid at  $-78.5^{\circ}\text{C}$ , so that it will provide rapid thermal conduction by convection. Although nonflammable liquids are preferable, acetone is commonly used for this purpose, but its mixtures with dry ice seem too prone to boil over suddenly without warning, intensifying the fire hazard. Diethylether gives very satisfactory cooling mixtures, and, since the vapor pressure of ether at  $-78.5^{\circ}\text{C}$  is less than 1 mm, evaporation from an open Dewar flask containing such a mixture is not hazardous. Other less flammable liquids, such as those described in a later section on

"Cooling Baths," may be used, provided they are sufficiently fluid at dry ice temperature.

In the preparation of a dry ice-liquid medium bath, the pulverized dry ice may be added to the liquid in a Dewar flask, or vice versa; in either case, the ingredients must be mixed very slowly because of the large amount of carbon dioxide gas liberated in cooling the liquid down from room temperature. When such a bath is used for cooling a tube, the tube should be immersed slowly to prevent such rapid evolution of gas as to cause the cooling mixture to overflow.

It should be pointed out here that dry ice may be colder than its equilibrium sublimation temperature, and the temperature should be measured if its exact value is important to the operation. The equilibrium temperature is that at which solid carbon dioxide has a vapor pressure equal to the partial pressure of the carbon dioxide vapor in the atmosphere immediately adjacent to the surface of the solid. This partial pressure will not be equal to 1 atmosphere if air is mixed with the carbon dioxide. An initial temperature of freshly crushed dry ice in a Dewar flask has been reported <sup>5</sup> as about  $-87^{\circ}\text{C}$ , and the normal sublimation temperature was not reached until about 10 hours had elapsed. When liquids are used as media, the mixtures do not behave very differently from solid carbon dioxide alone, all exhibiting an initial low temperature and a gradual temperature rise.<sup>6</sup> Furthermore, the equilibrium temperature of the mixture at a point below the surface is somewhat affected by the hydrostatic pressure at that point, so that it varies with the depth; this effect may be disturbed by convection. At the Bureau of Standards <sup>5</sup> the carbon dioxide sublimation point was found to be most quickly and conveniently produced by burying a small electrical heating coil in crushed dry ice in a Dewar flask, about 5 cm below the thermometer. In a few minutes at 30 watts, the temperature rose to  $-78.5^{\circ}\text{C}$ , and thenceforth 7 watts heat input was sufficient to maintain this temperature by keeping a steady stream of carbon dioxide evolving to exclude air.

<sup>5</sup> R. B. Scott, "The Calibration of Thermocouples at Low Temperatures," in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, p. 212.

<sup>6</sup> J. Zeleny and A. Zeleny, *Phys. Rev.*, **23**, 308 (1906).

**Liquid Ammonia.** Liquid ammonia, which is cheaply available commercially, is sometimes used directly as a cooling bath, because it maintains itself at its boiling point of  $-33.4^{\circ}\text{C}$  by evaporation, at 1 atmosphere pressure.

The chief advantage of this coolant is that it is colorless and very transparent, and its boiling point is sufficiently high that it does not bubble rapidly in a reasonably well evacuated Dewar flask. These properties make it very useful as a transparent coolant in an unsilvered glass Dewar flask, permitting clear visibility of a substance or reaction in a tube immersed in the bath.

The disadvantages are rather obvious. Since the low temperature is maintained by evaporation, liquid ammonia in open Dewar flasks releases ammonia gas into the air. Ammonia gas is of course extremely irritating to the eyes and to the upper respiratory tract, even in small concentrations. In larger concentrations, such as may easily be produced by spilling some of the liquid, ammonia gas practically paralyzes the breathing mechanism, so that it is not only irritating but dangerous. In liquid form, since it does not evaporate rapidly enough from the skin to form a gas cushion preventing wetting, it can cause painful freezing of human tissues.

The following precautions should therefore be observed when liquid ammonia is handled for use as a coolant. It should be exposed to the atmosphere only where there is good ventilation, preferably under a hood. Tubes to be cooled should be immersed in liquid ammonia slowly enough to prevent possibility of boiling over or splattering. In all work with this material, the eyes, and usually the hands, should be protected against splattering. More than one individual should be present whenever moderately large quantities of liquid ammonia are exposed to the atmosphere.

A material of similar boiling point which is said to be much more pleasant to use is the familiar refrigerant, dichlorodifluoromethane, *Freon-12*,\* b.p.  $-29.8^{\circ}\text{C}$ , which is nonflammable and practically nontoxic and odorless.

**Cooling Baths.** There are two types of cooling baths, one consisting merely of liquids cooled to the desired temperature by

\* Suggested by W. A. McMillan, private communication; obtainable from Kinetic Chemicals, Inc., Wilmington, Del.

some outside means, and the other consisting of materials which can maintain a constant temperature by a change of phase.

For the first type, all that is needed is a material which is very fluid at the desired temperature. Preferably this liquid should be quite volatile at room temperature to eliminate the necessity of cleaning the outside of apparatus which has been immersed in the bath. For temperatures down to  $-80^{\circ}\text{C}$ , a number of readily available liquids are suitable, such as ethyl alcohol, ether, and various mixtures. Nonflammable liquids are more desirable, and a number of organic halides have been investigated and recommended for temperatures down to  $-150^{\circ}\text{C}$ .<sup>7</sup> These are listed in Table II. For much lower temperatures, most liquids

TABLE II. NONFLAMMABLE LIQUIDS FOR COOLING BATHS

Weight %	Material	Minimum Temperature, $^{\circ}\text{C}$
100	Carbon tetrachloride	-23
100	Chloroform	-63
49.4	Carbon tetrachloride	-81
50.6	Chloroform	
100	Ethyl bromide	-119
19.7	Chloroform	-139
44.9	Ethyl bromide	
13.8	<i>trans</i> -1,2-Dichloroethylene	
21.6	Trichloroethylene	
14.5	Chloroform	
25.3	Dichloromethane	-145
33.4	Ethyl bromide	
10.4	<i>trans</i> -1,2-Dichloroethylene	
16.4	Trichloroethylene	
18.1	Chloroform	-150
8.0	Ethyl chloride	
41.3	Ethyl bromide	
12.7	<i>trans</i> -1,2-Dichloroethylene	
19.9	Trichloroethylene	

become too viscous, and the choice is more limited. It appears to be necessary to use flammable materials below  $-150^{\circ}\text{C}$ . Every effort should be made to avoid the possibility of accidentally mixing these materials with refrigerants containing liquid oxygen. Pentane is satisfactory down to about  $-160^{\circ}\text{C}$ , and

<sup>7</sup> C. W. Kanolt, *Natl. Bur. Standards (U. S.), Sci. Paper* 520, March, 1926.



propane down to liquid air temperatures.<sup>8</sup> Liquid propane (b.  $-42.1^{\circ}\text{C}$ ) may be obtained by passing propane gas from a cylinder, through a coil immersed in a dry ice bath, into a Dewar flask to contain it. A mixture containing 5.8 volumes of *n*-pentane, 2.2 volumes of methylcyclohexane, and 1.0 volume of *n*-propyl alcohol is described<sup>9</sup> as being liquid and fairly fluid down to  $-180^{\circ}\text{C}$ .

The second type of cooling bath requires a pure compound which can be partially frozen to form, preferably, a fluid slush, which will maintain the temperature of melting as long as any of the solid phase remains. The most common example is water-ice. Other materials which have been suggested<sup>10</sup> for use in maintaining constant temperatures are listed, with their approximate melting points, in Table III.

TABLE III. MATERIALS FOR CONSTANT LOW TEMPERATURE SLUSH BATHS

<i>Compound</i>	<i>M.P., °C</i>	<i>Compound</i>	<i>M.P., °C</i>
Eucalyptol	-2	Diamylnaphthalene	-30
Acetonyl acetone	-6	Dipropyl ketone	-33
Methyl salicylate	-9	Ethylene dichloride	-36
Diethylene glycol	-11	Diethyl ketone	-42
<i>t</i> -Amyl alcohol	-12	Tetrachloroethylene	-44
Benzaldehyde	-14	Chlorobenzene	-46
Diethyl carbonate	-15	Ethyl malonate	-50
Octyl alcohol	-18	Diacetone alcohol	-55
Butyl benzoate	-20	Amylnaphthalene	-60
Carbon tetrachloride	-23	Chloroform	-64
Diethyl sulfate	-25		

When more exact temperature baths are desired, the compounds listed in Table IV have been suggested<sup>11</sup> for use in pure state as low temperature standards, and hence may be used for cooling baths.

Slush baths are prepared by thoroughly stirring the liquid compound while cooling it to its freezing point. This breaks up the crystals as they are formed so that the final state resembles a mixture of snow and ice-water. If cooling is inadvertently con-

<sup>8</sup> A. Stock, *Ber.*, **53**, 751-758 (1920).

<sup>9</sup> G. Beck, *Deut. Z. ges. gericht. Med.*, **12**, 1 (1928).

<sup>10</sup> J. C. Bryan, *Chemist Analyst*, **29**, 71 (1940).

<sup>11</sup> J. Timmermans, *Bull. soc. chim. Belg.*, **32**, 95-96 (1923).

tinued to where the crystal-liquid mixture is too thick, the correct fluidity can easily be regained by adding, with stirring, a small additional quantity of the compound at room temperature.

TABLE IV. LOW TEMPERATURE STANDARDS

<i>Compound</i>	<i>M.P., °C</i>
Carbon tetrachloride	−22.9
Chlorobenzene	−45.2
Chloroform	−63.5
Ethyl acetate	−83.6
Carbon disulfide	−111.6
Methylcyclohexane	−126.3

## MEASURING LOW TEMPERATURES

Five different devices for measuring low temperatures are:<sup>12</sup> gas thermometer,<sup>13</sup> vapor pressure thermometer, liquid-in-glass thermometer, thermocouple, and resistance thermometer.<sup>14</sup> The simplest of these, the liquid-in-glass thermometer and the vapor pressure thermometer, are quite suitable for most chemical high vacuum work. Thermocouples with potentiometers are sometimes more readily available and are therefore used in place of vapor pressure thermometers.

**Liquid-in-Glass Thermometers.**<sup>15</sup> For the liquid-in-glass thermometer, toluene is considered suitable down to  $-95.1^{\circ}\text{C}$ , *n*-pentane to  $-131.5^{\circ}\text{C}$ , and isopentane to  $-159.7^{\circ}\text{C}$ .<sup>16</sup> Although, when calibrated against a secondary standard such as a platinum resistance thermometer, these thermometers are said to be reliable to  $0.1^{\circ}$ , in practice they often give trouble through breaking

<sup>12</sup> J. G. Aston and H. L. Fink, *Chem. Revs.*, **39**, 357–396 (1946).

<sup>13</sup> For a general discussion, see W. H. Kessom and W. Tuyn, *Commun. Phys. Lab. Univ. Leiden*, Suppl. 78 (1936); also F. G. Keyes in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, pp. 45–59; J. R. Roebuck and T. A. Murrell, *ibid.*, pp. 60–73.

<sup>14</sup> M. S. Van Dusen, *J. Am. Chem. Soc.*, **47**, 326–332 (1925); G. K. Burgess, *Bur. Standards J. Research*, **1**, 635 (1938).

<sup>15</sup> For a general discussion, see J. Busse, "Liquid-in-Glass Thermometers," in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, pp. 228–255.

<sup>16</sup> J. Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911).

of the liquid threads in the capillaries. Another disadvantage is that it is not always convenient to read them, as when they are immersed in a silvered Dewar flask.

**Vapor Pressure Thermometers.** Vapor pressure thermometers operate on the principle that pure compounds exert vapor pressure which is proportional only to the temperature. The pure compound is confined in a small space connected directly to an ordinary mercury manometer, which records the pressure corresponding to the lowest temperature to which the compound is subjected. Obviously these thermometers are suitable only for temperatures below that of the surroundings.

Various designs for vapor pressure thermometers have been suggested.<sup>17</sup> A simple, convenient form is shown in Figure 16. This thermometer is filled as follows: It is sealed to the vacuum line at A, and a dropping funnel is inserted at B; it is sealed with picein. The apparatus is very thoroughly evacuated and heated to remove all possible gases and vapors. When

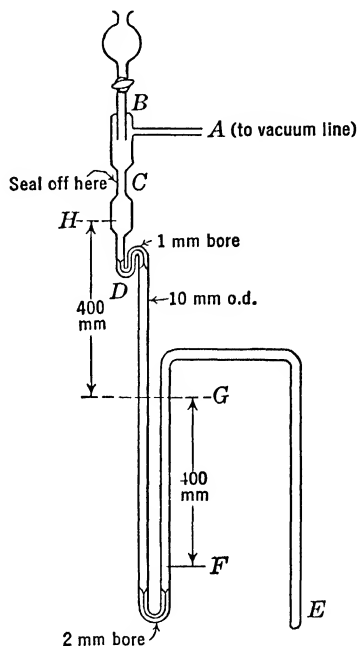


FIG. 16. Vapor pressure thermometer.

evacuation is as complete as possible and the apparatus is cool, a measured volume of the pure thermometric material, equal to the calculated volume of the tube from E to F at 800 mm pressure, is condensed in E by cooling with liquid nitrogen. Mercury is then added at B to fill the manometer up to G, the zero pressure point. Next, the thermometer is carefully sealed off at C. It is now ready for use. When the material at E is per-

<sup>17</sup> See, for example, A. Stock, *Z. Elektrochem.*, **29**, 354 (1923); W. Heuse and J. Otto, *Ann. Physik*, **9** [5], 486 (1931); A. Farkas and L. Farkas, *Ind. Eng. Chem., Anal. Ed.*, **12**, 296 (1940).

mitted to warm to room temperature, the top of the mercury column will be at *H*. Any gases liberated from the glass by sealing off at *C* are thus contained above the capillary *D*. When the thermometer is used, cooling at *E* causes the mercury to drop through the capillary *D*. By tapping the capillary as the last part of the mercury is running through, the mercury thread may be broken, leaving a mercury seal in the capillary between any desorbed gases above and the Torricellian vacuum below.

The compounds listed in Table V are useful for filling vapor pressure thermometers.<sup>18</sup>

TABLE V. COMPOUNDS FOR VAPOR PRESSURE THERMOMETERS

<i>Compound</i>	<i>Temperature Range, °C</i>
Carbon disulfide	25 to -10
Sulfur dioxide	-10 to -40
Ammonia	-30 to -77
Carbon dioxide	-75 to -100
Hydrogen chloride	-85 to -111
Ethylene	-100 to -150
Methane	-150 to -185
Oxygen	-180 to -200

These compounds may be prepared as follows:

*Carbon disulfide.* Commercial carbon disulfide may be purified by fractionation in the high vacuum line.

*Sulfur dioxide.* Concentrated sulfuric acid is dropped into a concentrated solution of pure sodium sulfite in an evacuated flask. The gas is dried with  $P_2O_5$  and fractionated.

*Ammonia.* Commercial synthetic ammonia needs only drying with sodium (see page 97) and separation from the hydrogen evolved.

*Carbon dioxide.* Carbon dioxide may be prepared by heating, in vacuo, pure sodium bicarbonate and drying the gas with  $CaCl_2$  and  $P_2O_5$ .

*Hydrogen chloride.* Pure concentrated hydrochloric acid is dropped into warm sulfuric acid in a vacuum system, and the HCl is dried with  $P_2O_5$ .

*Ethylene.* Ethylene is prepared by heating orthophosphoric acid to 200°C in an evacuated system and slowly adding ethyl alcohol. The product may be purified by fractionation.

<sup>18</sup> F. Henning and A. Stock, *Z. Physik*, **4**, 227 (1921).

**Methane.** Methane may be prepared by hydrolysis of a methyl Grignard solution and fractionation of the product.

**Oxygen.** Pure potassium permanganate is heated in an evacuated tube, first at 160–175°C for several hours to remove sorbed air, and then slowly to 215–235°C, the first portion of evolved oxygen being discarded. Traces of carbon dioxide may be removed by soda lime.

The vapor pressure-temperature relationships for the above compounds are given in the Appendix, page 117.

**Thermocouples.** Low temperatures may be determined with a usually satisfactory degree of accuracy by use of thermocouples, provided the limitations and requirements are adequately understood.

The principle of thermoelectric temperature measurement is based on the well-known discovery<sup>19</sup> that an electric current flows continuously in a closed circuit of two unlike metals when the junctions of the metals are maintained at different temperatures. A thermocouple consists of just such a circuit, and the temperature difference between the junctions is determined by measuring the emf created, with a suitable instrument such as a potentiometer.<sup>20</sup> The magnitude of the thermoelectric effect obtained with commonly used metal combinations ranges from about 1–7 millivolts for a 100°C temperature difference between junctions. One junction must be maintained at a constant reference temperature, so that the temperature at the other junction can then be determined. Frequently the constant reference temperature is 0°C, conveniently obtained by immersing the proper junction in an ice-water bath. However, modern instruments are usually equipped with automatic reference junction compensators, which change the indication of the instrument to correct for changes in the temperature of the reference junction,

<sup>19</sup> T. J. Seebeck, *Gilb. Ann.*, **73**, 115, 430 (1823); *Pogg. Ann.*, **6**, 1, 133, 253 (1826).

<sup>20</sup> For detailed discussions, see W. P. White, "Potentiometers for Thermoelectric Measurements," in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, 265–278; T. J. Rhodes, *Industrial Instruments for Measurement and Control*, McGraw-Hill Book Co., Inc., New York and London, 1941, pp. 128–140; H. C. Roberts, *Mechanical Measurements by Electrical Methods*, The Instruments Publishing Co., Inc., Pittsburgh, 1946, pp. 230–236.

and thus make measurement or control of the reference junction temperature unnecessary.

Copper-constantan thermocouples, which are satisfactory from  $-200$  to  $350^{\circ}\text{C}$ , are the most commonly used thermocouples for determining temperatures ranging from ice to liquid nitrogen. *Constantan* is a general name covering a group of alloys containing 45–60% of copper and 40–55% of nickel (with or without small percentages of manganese, iron, and carbon). The thermocouple wires may range in size from No. 22 to No. 36 B & S gage.

For most precise measurements, such thermocouples are calibrated for this low temperature range ( $-200^{\circ}$  to  $0^{\circ}\text{C}$ ) by direct comparison with a platinum resistance thermometer, but sufficient accuracy for most purposes may be obtained by calibrating at just two temperatures, the carbon dioxide sublimation point and the oxygen boiling point.<sup>21</sup> Since neither of these points is easily reproducible with precision, the temperatures of the dry ice and liquid oxygen baths should be measured exactly. For this purpose, vapor pressure thermometers containing carbon dioxide and oxygen, respectively, are convenient. A deviation curve, showing how the thermocouple being calibrated differs from a standard copper-constantan thermocouple for which very accurate data are available, may then be constructed. The deviations of the observed emf's from those given in the reference table (page 121) for the standard are plotted as ordinates versus the observed emf's as abscissa, and a smooth curve connecting these points with the  $0^{\circ}\text{C}$  point is drawn. A table correlating the actual thermocouple emf's with temperature can then be compiled for use with that particular thermocouple.

It is stated that the accuracy with which copper-constantan thermocouples may be calibrated for use at low temperatures is usually limited by lack of homogeneity of the wires. Copper is relatively uniform. Constantan may be quite variable. It is generally accepted that a closed circuit of entirely homogeneous metal will exhibit no thermal potential regardless of thermal differences in the circuit. Any observed emf is ascribed to irregularities in the chemical composition or physical condition of

<sup>21</sup> R. B. Scott, "The Calibration of Thermocouples at Low Temperatures," in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, 206–218.

the wire material. This affords a means of selecting constantan which is adequately uniform for accurate thermocouples: Check it for emf's produced by large temperature differences in a closed circuit, and choose a length where such effects are negligible. Sometimes an attempt is made to cancel out inhomogeneities in constantan by using several constantan wires in parallel, attached in a single junction to the same copper wire. For example, three No. 30 B & S double-silk-insulated constantan wires and a single No. 36 B & S copper wire have been used.<sup>22</sup>

Calibration as described above should be accurate to about  $\pm 2$  microvolts (maximum less than 4), which is all that is justified in view of the probable inhomogeneities in the wires. This would correspond to about  $\pm 0.12^\circ\text{C}$  at  $-190^\circ\text{C}$  and  $\pm 0.06^\circ\text{C}$  at  $0^\circ\text{C}$ . In general, unless extreme care is taken, the accuracy of the temperature determinations in which a copper-constantan thermocouple is used is expected to be about  $\pm 0.3^\circ\text{C}$ .<sup>23</sup>

Once a thermocouple has been constructed and properly calibrated, it may be used indefinitely for low temperature measurement. No indications of appreciable changes over several years have been observed.

It is often desirable to enclose thermocouples in a protective sheath. Such a sheath should be thin-walled and close fitting, but at best the sensitivity of the thermocouple to changing temperatures is diminished, especially if the sheath is of glass. Thermal transfer may be much improved by imbedding the thermocouple in copper dental cement within the sheath.†

<sup>22</sup> J. G. Aston, "The Use of Copper-Constantan Thermocouples for Measurement of Low Temperatures Particularly in Calorimetry," in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, p. 219.

<sup>23</sup> W. F. Roeser and H. T. Wensel, "Methods of Testing Thermocouples and Thermocouple Materials," in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, p. 311.

† H. D. Baker, Columbia University, private communication. Technical B Copper Cement is obtainable from Weinbaum Dental Supply Co., 220 W. 42nd St., New York, N. Y.

## *Valves*

### STOPCOCKS

For relatively large scale chemical work, involving, for example, several milliliters or more of liquid, stopcocks may be used throughout a vacuum system with reasonably good success. The main advantage is that they are very easy to open and close. There are certain disadvantages, however, which make stopcocks relatively undesirable for smaller scale and more careful high vacuum work. First, they are always potential sources of leaks. Second, they must be lubricated with greases which may react chemically with materials handled in the system, or which may dissolve small amounts of those materials, liberating them into a vacuum so slowly as to interfere with attainment of the desired low pressures. Third, they may not be heated, because of the danger of driving out or thinning the lubricant or actually breaking the stopcock. This means that the tubing next to the stopcocks may not be heated for the purpose of aiding in degassing the system.

Because of their ease of operation, which is independent of any pressure differential, it is convenient to use stopcocks between the pumping system and the vacuum apparatus and between the vacuum apparatus and the atmosphere. It is desirable, however, to be able to shield the stopcock lubricant from contact with vapors in the apparatus. This is accomplished by means of a mercury cut-off, such as that illustrated in Figure 17. The stopcock is mounted in a small U-tube which is supplied with mercury from a pressure-vacuum-operated reservoir. The *D* side of the stopcock is connected to pump or atmosphere, and the *C* side is connected to the vacuum system. To close the valve, the stopcock is closed and mercury is run into the U-tube by



opening the reservoir to the atmosphere. To open the valve, the mercury is allowed to fall back out of the U-tube by opening the reservoir to a rough vacuum, and then the stopcock is opened. Failure to lower the mercury before opening the stopcock may result in blowing the mercury into parts of the apparatus where it is not wanted. If the mercury is not run all the way to the stopcock when the valve is closed, the valve may be utilized also as a low range manometer.

For high vacuum work, stopcocks as well as all other ground joints should be sufficiently well made to be completely sealable from leakage by a very thin and uniform film of lubricant. Modern ground joints are ordinarily manufactured sufficiently well. When a thin lubricant coating does not give a clear, transparent film maintaining its clarity during relative motion of the ground joint parts, the joint is much more likely to be a source of leaks. Faulty joints should therefore be ground to closer fit by carefully working them together with a slurry of very fine emery powder and water.

### MERCURY FLOAT VALVES

Numerous greaseless valves have been proposed for high vacuum work.<sup>1</sup> For general chemical work, the mercury float valve<sup>2</sup> is quite satisfactory. A useful modification of one is shown in Figure 17. It consists of a small U-tube connected between the parts of the apparatus to be closed from each other. Each arm of the U-tube contains a glass float with a ground, tapered tip which fits a ground joint in the arm. When the valve is open, the floats rest on glass supports formed by indenting the tube. The valve is closed by forcing mercury from the reservoir into the U-tube, where it floats the plugs into place. Light tapping with the fingers at the joint helps to insure proper seating

<sup>1</sup> See, for example, A. Stock, *Ber.*, **58B**, 2058–2060 (1925); M. Bodenstein, *Z. phys. Chem.*, **B**, **7**, 387 (1930); H. C. Ramsperger, *Rev. Sci. Instruments*, **2**, 738–749 (1931); J. Willard, *J. Am. Chem. Soc.*, **57**, 2328 (1935); O. Krieg, *Z. tech. Physik*, **23**, 314–315 (1942); W. E. Vaughan, *Rev. Sci. Instruments*, **16**, 254–255 (1945).

<sup>2</sup> A. Stock and O. Priess, *Ber.*, **47**, 3109–3113 (1914). For modifications, see A. Stock, *Z. Elektrochem.*, **23**, 33–35 (1917); H. Ramser and E. Wiberg, *Z. Elektrochem.*, **36**, 253 (1930); H. Lux, *Z. anorg. allgem. Chem.*, **226**, 21–22 (1935).

of the floats as they are lifted into position. The ground joints should be so constructed that they permit no leakage of mercury under a pressure differential of at least 1 atmosphere. These float valves can be built by any competent professional glass blower. They are very useful in high vacuum systems since they

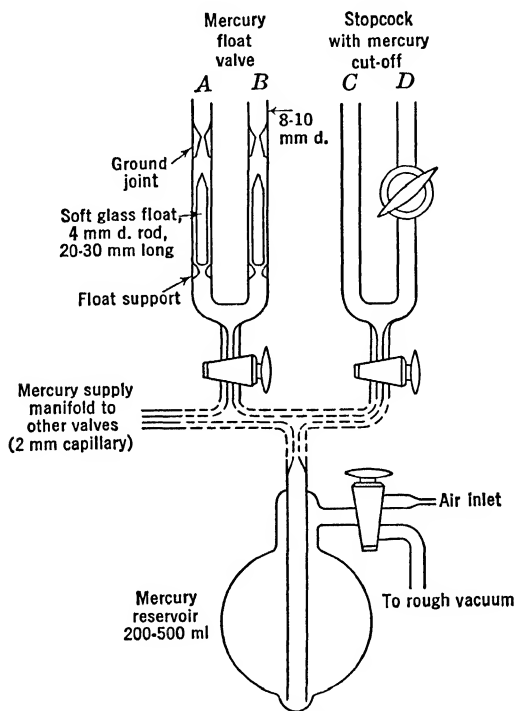


FIG. 17. Valves.

may be thoroughly degassed by heating, and they have exposed surfaces only of glass and mercury.

The earlier modifications of this valve had the disadvantage that they could not be opened under an appreciable pressure differential. Thus, if the A side of the float valve in Figure 17 were at a pressure of 1 atmosphere and the B side of less than 1 millimeter, an attempt to open the valve by lowering the mercury would result in immediate jamming of the mercury against the float in side B. With all the mercury withdrawn, the float would still be held tightly in the joint by the gas pressure, and

it could not be removed from the joint until the pressure had been equalized by very slow leakage of the gas.

To avoid this difficulty, where the pressure differential cannot be removed by cooling the gas on the pressure side or admitting gas to equal pressure on the vacuum side, the floating plugs are made of soft glass.<sup>3</sup> These plugs make it possible to open the valve under a pressure differential, as follows: The closed joint on the pressure side A is warmed very carefully with a low gas flame. Owing to the much greater coefficient of thermal expansion of the soft glass, the plug expands within the joint and sticks there. The minimum heat should be used to avoid cracking the joint. This heat can be determined by heating gradually until the mercury can be lowered without causing the plug to fall. (This, incidentally, is not so hazardous as it may seem; the possibility of breaking a well-annealed joint of this kind by heating with a low, carbon flame of a gas burner is quite slight.) The joint is kept warm while the mercury is completely withdrawn. The float on the vacuum side, of course, falls promptly, and the float on the pressure side falls to open the valve completely as soon as the joint has cooled.

## MERCURY RESERVOIRS

Often mercury valves are constructed with individual reservoirs of mercury. As long as these are not open to the air, creating a mercury vapor hazard, this is quite satisfactory. However, it has been found very convenient to use a single large reservoir to supply all valves which are at approximately the same level. Such a reservoir minimizes the number of more expensive three-way stopcocks which must be used and saves space by requiring only a manifold supply line, made of 2-mm bore capillary, to bring mercury to and from the valves. It is desirable, for ease of making repairs, for all lines from the valves to be sloping slightly toward the reservoir, so that the supply manifold can be completely drained if necessary.

A typical reservoir is shown in Figure 17. A useful base for supporting such a reservoir may be constructed of plaster of Paris, as described on page 45.

<sup>3</sup> A. B. Burg, *J. Am. Chem. Soc.*, **56**, 499 (1934).

## *Introducing into and Removing from Vacuum System*

In experimentation using a high vacuum system, it is sometimes desirable to be able to introduce materials to the system or remove them from the system without losing the vacuum or allowing the materials to come in contact with air. To accomplish these ends, various techniques have been devised.

For some of these techniques, it is convenient to have a special small part of the high vacuum system devoted to temporary installations requiring admission of air. This part consists of a section of tubing connected to the main system by a mercury float valve, and with independent connections to the pumping system. It may contain a dry air inlet, a tube opener (to be described presently), a U-tube trap, and open arms where miscellaneous tubes may be attached by use of picein. When not in use, these openings are closed with picein-sealed glass plugs.

### TRANSFER TUBES AND TUBE OPENER

Removal of materials from a vacuum system usually involves condensing the material in a tube by cooling, and sealing the tube off from the system by use of the glass-blowing torch. In Figure 18 is shown a type of tube useful for taking a material out of a system and later putting it back. It is constructed in any desired form, provided that at least part of it will fit within a Dewar flask, and has a side arm drawn to a thick-walled capillary tip and a thick-walled constriction for sealing off at *B*. The capillary tip should be made with care; the end should be melted and blown out several times to make sure that a tiny hole is not left at the very point. The walls of the capillary must be strong

enough to resist breakage by careless handling, and thick enough to receive a file scratch without collapsing.

To remove a material from the vacuum system, dry air is admitted to the side line, which is kept closed to the main system. A plug is removed from an opening, and a tube of the type described above is sealed to the opening (at A in Figure 18) with picein. The side line is then pumped out thoroughly, both tube

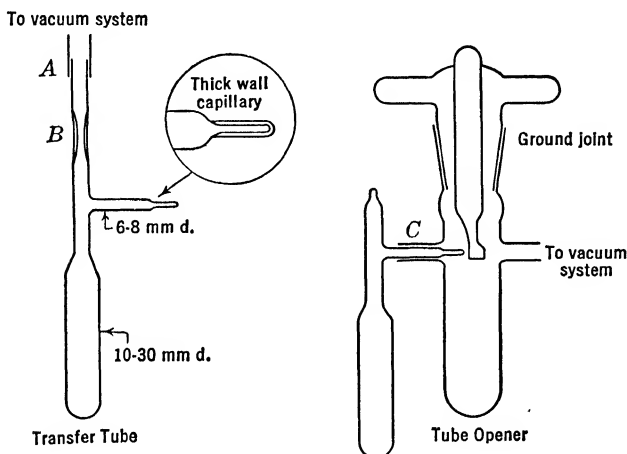


FIG. 18. Transfer tube for storage and reaction outside of vacuum system, and tube opener for admitting contents to vacuum system.

and wax seal being tested for leaks with a Tesla coil. It is closed to the pump and opened to the main system through the connecting float valve. The tube to be filled is cooled to the necessary low temperature, and the material is allowed to diffuse into it from the main line. When this transfer is complete, the tube is carefully sealed off at B, as described on page 27. The picein may be shielded from the heat by wrapping the joint in wet cotton. The wet cotton should not be allowed to become very warm to the touch, or there will be danger of the picein softening and sucking in at the joint. Neither should the cotton be too wet, or water might run down over the heated glass.

Such tubes are very useful for removing materials for storage or for reaction outside the vacuum system. For example, reactants may be measured in the system, condensed together in

the tube and sealed from the line, and then subjected to more drastic heating than possible within the system. For any reaction wherein a pressure exceeding 1 atmosphere could conceivably develop, the tube should be well shielded. (See also page 97.)

When the contents of such a tube are to be returned to the vacuum line, use is made of a tube opener<sup>1</sup> such as that illustrated in Figure 18. Air is admitted to the side line, and a plug is removed from the side arm of the tube opener at C. Next, the ground joint is turned to test the functioning of the lubricant. A file scratch is carefully made then, on the capillary tip of the storage or reaction tube, and the side arm of the tube is inserted in the side arm of the tube opener and sealed with picein in such a position that the tip in front of the file scratch can be snapped off by rotation of the breaker handle. In order to avoid breaking the picein seal by pressure to be exerted on the tip by the breaker, it is advisable to choose tubing for the tube side arm which will fit closely the inside of the tube opener side arm, and to seal the tube in such a way that pressure against the tip will be borne by glass rather than by wax. In other words, before it is sealed in place, the tube side arm should be twisted to a firm position in the tube opener side arm in the direction in which stress will be applied by the breaker. After sealing, air is pumped out thoroughly and the seal tested for leakage, and the side line is closed to the pumps and opened to the main line. The contents of the tube are condensed by cooling, and then the breaker is rotated to snap off the capillary tip. The tube contents are then allowed to warm and distill over into the vacuum system, to be condensed there at whatever place desired.

The same tube may be used for several successive removals and returns of materials if several more side arms with capillary tips are added and if the proper spaces for sealing off are provided.

### WEIGHING TUBES

When volatile materials are to be removed for weighing, tubes of the types shown in Figure 19 are useful. For those tubes which have stopcocks, provision is made, by the short side arm

<sup>1</sup> A. Stock, *Ber.*, **51**, 985 (1918).

A which contains a small amount of mercury, for shielding the stopcock lubricant from contact with the contents of the tube. The procedure is as follows: The weighing tube is sealed with picein to an opening of the vacuum side line, and the system is thoroughly evacuated. The weigh bulb is heated to remove sorbed gases, the picein joint and the stopcock being protected against overheating. The side arm A containing the mercury

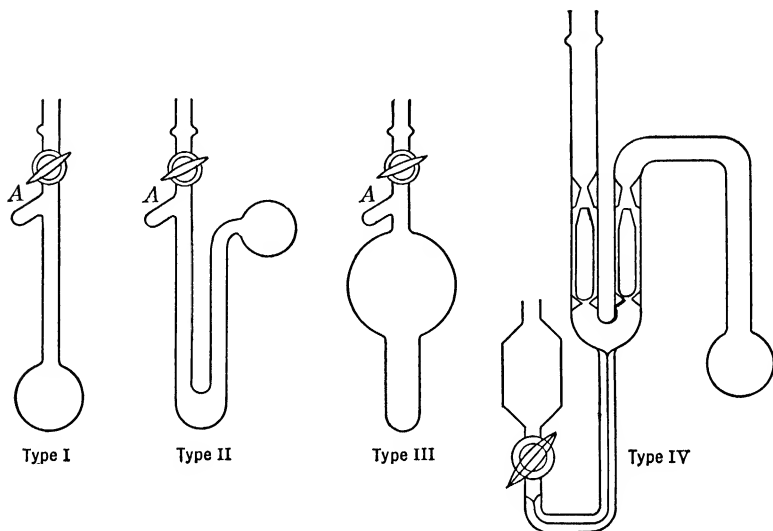


FIG. 19. Gas-weighing tubes.

must be warmed very cautiously, and in fact even evacuated cautiously, being tapped lightly, to avoid sudden pushing out of the mercury by a bubble of desorbed gas, which would require disconnecting and inverting the tube to return the mercury to the side arm. When evacuation is complete, the bottom of the weighing tube is cooled with liquid nitrogen, and the sample to be weighed is allowed to condense there. The sample is thus momentarily exposed to stopcock lubricant. When condensation is complete, the stopcock is closed, air is admitted to the side line, and the weighing tube is removed by melting the picein, and immediately removed from the cooling bath and inverted. This procedure allows the mercury to cover the stopcock before the contents have vaporized in the tube. Picein is cleaned off

completely. When the tube has reached room temperature and is free of condensed moisture on the outer surface, it is weighed. The tube is then turned, stopcock up, and cooled immediately to condense the contents. To eliminate even this momentary contact with the stopcock lubricant, the contents may be condensed before the tube is turned, by applying a piece of cotton moistened with liquid nitrogen to the glass first. After the tube is attached to the side line again, it is emptied by returning the contents to the vacuum system, and removed as before and weighed again evacuated. The difference between the two weights, of course, represents the weight of the sample.

Of the weighing tubes shown in Figure 19, Type I is satisfactory for ordinary purposes, but small for very volatile materials which at room temperature would exert a dangerously high pressure in the small volume provided. Type III is simply a modification to take care of such materials by providing more space. Type II is useful for weighing materials which may decompose very slowly, or hydrolyze with minute traces of moisture in the system, to give noncondensable gas such as hydrogen. When even a very minute trace of noncondensable gas is present, it impedes greatly the diffusion of the condensable material, and quantitative condensation in a dead end tube is extremely difficult. Condensation in a part of the tube separate from the closed end is easier to complete in such a case. If it is necessary to avoid entirely the use of a stopcock, a weighing tube with a small mercury float valve attached, like Type IV, is useful.

As a check on the completeness of transfer of a vapor to a weighing tube, it is advisable to measure the volume of the vapor both before and after weighing.

## INTRODUCING NONVOLATILE MATERIALS

Where grease-lubricated ground joints are not objectionable, nonvolatile solids and liquids may be added to a reaction tube in vacuo by use of the familiar principle illustrated in Figure 20. The tube containing the nonvolatile material is simply rotated about the ground joint until the contents fall into the reaction tube by gravity.



## REMOVING MATERIALS FOR DISCARDING

Frequently it becomes desirable to remove materials from the vacuum system for discard, without pumping them out through the pumps, where they may contaminate the oil and pollute the atmosphere. For such purposes, it is useful to have a removable U-tube trap, equipped with stopcocks, like that shown in Figure 21, which may be connected to the main line through a float valve and to the pumps through a stopcock. An air inlet is also provided. It is then only necessary to close other valves to the pumps and pump the waste material from the main system through the chilled trap. When all the waste is condensed in this trap, this small section is closed to both pumps and line,

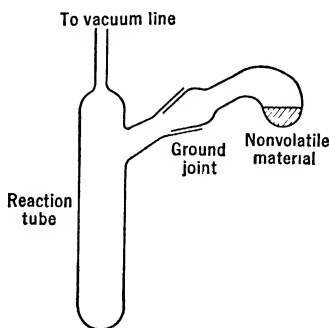


FIG. 20. Type of apparatus for adding nonvolatile materials in vacuo.

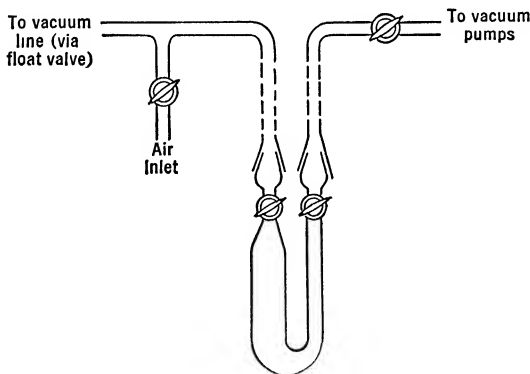


FIG. 21. Removable trap system.

the stopcocks of the trap are closed, and air is admitted to facilitate removal of the trap.

Alternatively, waste material may be condensed in any tube sealed to the side line by picein, and removed while frozen.

## *Measuring Volume*

Materials handled in a high vacuum system can be measured much more conveniently by gas volume than by weight. Any material which is sufficiently volatile to be studied in a vacuum system can be measured in terms of gas volume by appropriate means.

### NONCONDENSABLE GAS

A gas which cannot be condensed completely by liquid nitrogen requires special handling in a vacuum system, since it must be pumped from place to place. The most common gases of this type are nitrogen, oxygen, hydrogen, carbon monoxide, and methane.

A useful device for pumping noncondensable gas into any desired vessel, and particularly into a gasometer where its volume can be measured, is the Töpler pump. A suitable form for use in the high vacuum system is shown in Figure 22. The principle of operation is simple. An evacuated chamber which is first opened to the noncondensable gas is then filled with mercury, which forces the gas in this chamber over into a gasometer, or gas buret. Mercury is then withdrawn from the chamber, which is allowed to fill with noncondensable gas again, and the cycle is repeated. If the volume of the chamber is, for example, one-third of the total volume of the system, each cycle of the pump will move into the gasometer one-third of the remaining noncondensable gas.

The gasometer illustrated may be constructed from an ordinary Pyrex gas buret and calibrated before assembly by weighing measured volumes of mercury.

Initially, all the mercury is contained in the reservoir. The entire system is thoroughly evacuated with heating. Then the

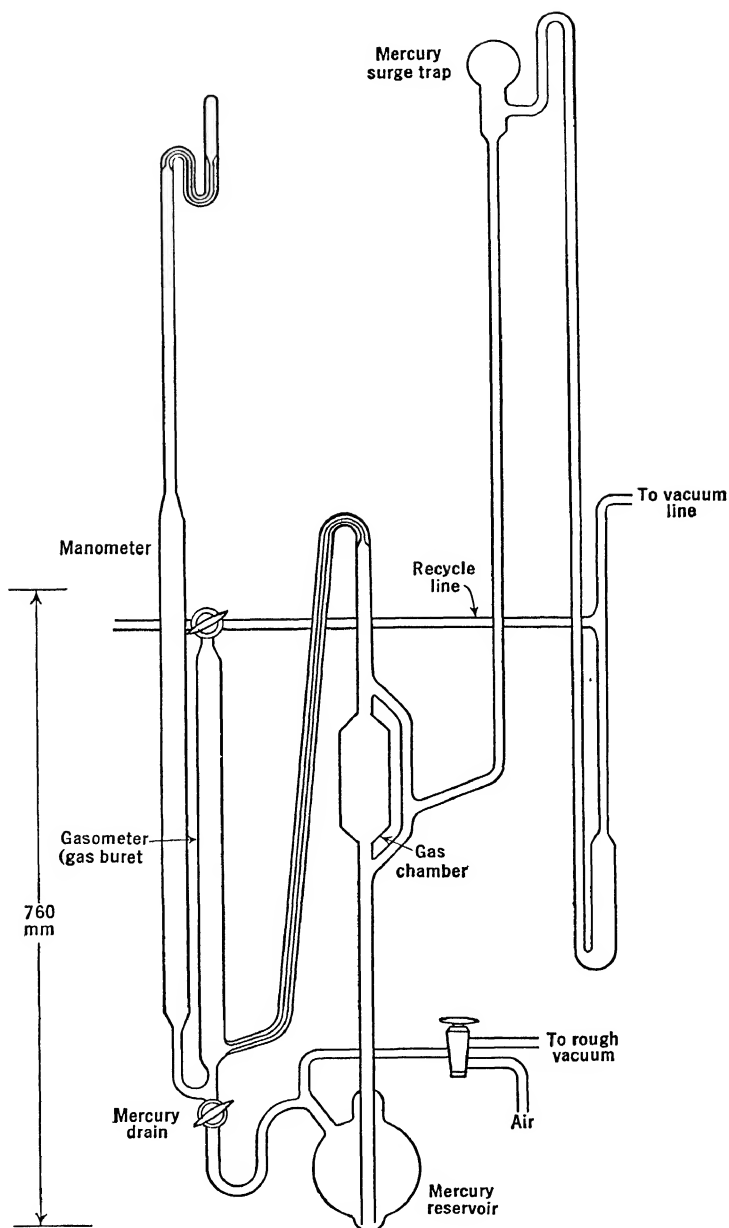


FIG. 22. Töpler pump and gasometer system.

mercury is forced up through the gas chamber by opening the reservoir to the atmosphere and supplementing atmospheric pressure by applying compressed air from a hose held to the air inlet. Mercury is forced over through the capillary at the top of the gas chamber into the gasometer and manometer until the gasometer is full. The trap is immersed in liquid nitrogen. The Töpler system is now ready for operation.

The system is opened to that part of the vacuum line which contains the noncondensable gas. All unnecessary parts of the apparatus should be kept closed to minimize the volume of space from which the noncondensable gas must be removed by pumping. The mercury is drawn down out of the gas chamber by applying a rough vacuum at the reservoir. It is then forced up again and over into the manometer, pushing the gas ahead of it into the gasometer. Then it is drawn back to the reservoir. A cushion of gas in the buret now having been provided, it is safe to drain most of the mercury out of the buret so that the pump may operate against less pressure. This is done by opening the stopcock at the bottom of the buret, until the mercury in the buret has fallen to a level just above the capillary inlet. It is important never to open this stopcock when the reservoir is at atmospheric pressure, in which case air would bubble up into the manometer and buret, possibly breaking both by the sudden upsurge of the mercury column.

Subsequent strokes of the pump are carried out by forcing the mercury behind the gas only a little way into the buret, draining it to a low level every few strokes. When the pumping appears to be complete, as determined by observation that no bubbles of gas are being carried through the capillary by each stroke, the volume may be measured. If there is a possibility that the noncondensable gas may have entrained condensable material and carried it through the trap into the gasometer, it is advisable to recycle the gas through the trap. This is accomplished by closing the Töpler system to the rest of the apparatus, opening the stopcock at the top of the gasometer to the recycle line, and circulating the gas a few times through the trap by use of the Töpler pump. This stopcock is then closed and the gas pumped back into the buret as before.

By adjusting the mercury levels in the buret and manometer, a series of pressure and volume readings may be made as checks, a meter stick being used for reading the pressures. The volume is converted to the volume at standard conditions by application of the ideal gas laws:

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

where  $V$  is the volume at standard conditions,  $P$  is always 760 mm (of Hg at 0°C), and  $T$  is always 273.16°K (0°C). Calculation of the standard volume may therefore be simplified by use of the factors given in Table VI:

$$V = V'P'F$$

$V'$  is the observed volume,  $P'$  is the observed pressure (in mm Hg at the temperature of observation), and  $F$  is a factor calculated from the expression

$$F = \frac{273.16C}{760T'}$$

where  $C$  is a correction factor for the thermal expansion of mercury and  $T'$  is the temperature (°K) of observation.

TABLE VI. FACTORS FOR CALCULATION OF VOLUMES AT STANDARD CONDITIONS

[Volume at 0°C, 760 mm, equals observed volume times observed pressure (mm Hg) times  $F$ ]

°C	$F$	°C	$F$
15	0.00124393	26	0.00119578
16	0.00123937	27	0.00119156
17	0.00123486	28	0.00118748
18	0.00123049	29	0.00118332
19	0.00122603	30	0.00117917
20	0.00122160	31	0.00117506
21	0.00121721	32	0.00117097
22	0.00121284	33	0.00116703
23	0.00120862	34	0.00116300
24	0.00120431	35	0.00115899
25	0.00120004		

The number of cycles required for substantially complete transfer of a noncondensable gas to a gasometer obviously depends on the ratio of the volume of the chamber to the total

volume of the system. If the initial gas pressure in the system is 10 mm, and the chamber volume is one-third of the total volume, 10 cycles of the pump will reduce the pressure to 0.17 mm, and 30 cycles to  $5 \times 10^{-5}$  mm. If the pump chamber is only one-tenth of the total volume, the pressure will only be reduced from 10 mm to 3.5 mm by 10 cycles, and it will still be 0.4 mm after 30 cycles. Although it is desirable for the gas chamber to be as large as possible to provide for maximum pumping speed, it is well to bear in mind that the pump must handle a correspondingly large weight of surging mercury, and therefore the dimensions must be kept consistent with the strength of the glass.

Manual operation of the Töpler pump is somewhat tedious, although restful, and numerous automatic modifications have been devised.<sup>1</sup> Since ordinarily the high vacuum system discussed herein is used primarily to handle condensable materials, manual Töpler pumps are satisfactory for occasional use.

It should be mentioned here that the Töpler system described above provides means not only of measuring a volume of non-condensable gas, but also of circulating such a gas through a reaction zone or transferring a measured sample quantitatively into a container, by forcing it from the gasometer into such a container connected at the top of the gasometer. Such uses will be described further on page 103.

### CONDENSABLE GAS

Volumes of condensable materials may be measured at room temperature if they exert enough vapor pressure, or at higher temperatures if necessary. The general procedure is simply to measure the temperature and the pressure exerted in a container of known volume and convert to the volume corresponding to standard conditions.

In general, gas volume measurements are subject to error due to sorption on the walls of the container. Ordinarily, however, this is not serious. Ammonia appears to be more readily sorbed

<sup>1</sup> B. D. Steele, *Chem. News*, **102**, 53 (1910); *Phil. Mag.*, **19**, 863 (1910); F. Porter, *Ind. Eng. Chem.*, **16**, 731-732 (1924); A. Stock, *Z. Elektrochem.*, **23**, 35 (1917); A. T. Williamson, *Rev. Sci. Instruments*, **3**, 782-789 (1932).

than most of the common gases, yet the volume sorbed on the walls of a 1-liter vessel at atmospheric pressure and room temperature amounts to only about 0.2 ml,<sup>2</sup> which would lead to an error of about 0.02 per cent.

Other errors are to be expected from deviations from the perfect gas laws. Such deviations may be minimized by measuring volumes at relatively low pressures, for example  $\frac{1}{2}$  atmosphere or less, and at temperatures well above the liquid-vapor equilibrium temperatures corresponding to the pressures of measurement.

**Volumes at Room Temperature.** For measuring gas volumes at room temperature, an ordinary U-tube trap, connected with a mercury manometer of calibrated bore, is quite satisfactory. Such a device is shown in Figure 23. The manometer is constructed of uniform tubing of about 10 mm diameter whose inside dimensions have been determined before construction by weighing a column of mercury of measured length therein. The volume of the U-tube and connecting tubing up to the closed float valves, which isolate the tube from the rest of the vacuum apparatus, may be determined, for zero pressure, as follows: The tube is opened to the vacuum line, and dry air is admitted to a pressure of, for example, 100–500 mm. The tube is then closed, and the air is pumped out of the rest of the system. The pressure and the temperature of the air in the tube are then carefully measured. The tube is then opened to the Töpler pump system, the method of opening the float valve described on page 65 being used, and the air is pumped into the gasometer and measured. This volume is converted to the volume corresponding to the pressure in the U-tube, which is the volume of the U-tube at that pressure. To find the volume of the U-tube at zero pressure, the volume due to the manometer beyond the zero point (which equals one-half the pressure in millimeters times the volume per millimeter) is subtracted. The zero pressure volume thus determined may be checked by similar calibration with different volumes of air; checks should be readily obtainable within 0.1 ml.

<sup>2</sup> J. W. McBain, *Sorption of Gases and Vapors by Solids*, George Routledge and Sons, Ltd., London, 1932, pp. 242–243.

An alternative method is to weigh a sample of a pure gas such as carbon dioxide which has exerted a measured pressure

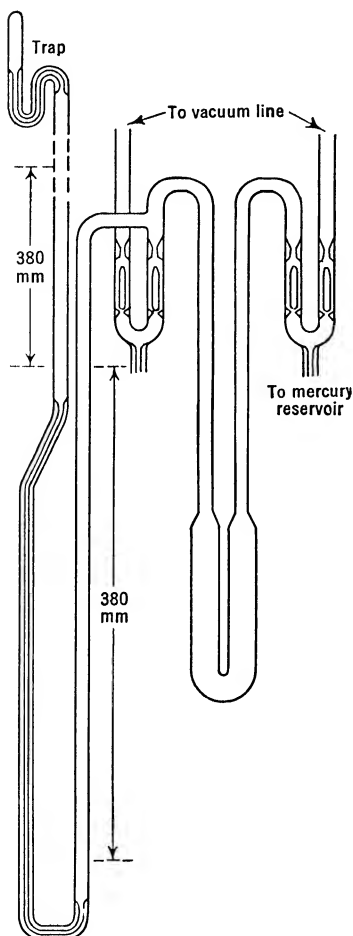


FIG. 23. Calibrated U-tube-manometer system.

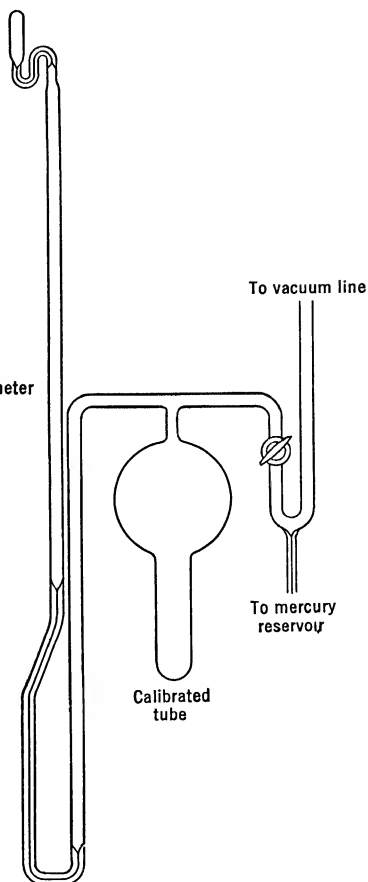


FIG. 24. Apparatus for measuring exact volumes.

in the U-tube. From the weight and the molecular weight, the volume can readily be calculated.

A U-tube trap may be suitable for volumes up to about 100 ml, but larger tubes, such as bulbs with an appendage narrow



enough to fit into a Dewar flask, are recommended for larger volumes. For volumes of only a few milliliters, a U-tube of about 10 ml volume is satisfactory. Very small volumes, ranging from 1 to less than  $10^{-4}$  ml, can be measured in a *microvol*.<sup>3</sup>

Often in studies of volatile compounds it is desirable to measure out calculated volumes exactly. For such purposes, mercury float valves are quite inconvenient, as they do not permit ready adjustment of volumes by slow and carefully controlled vapor leakage. For example, suppose that a volume of vapor that will exert a pressure of 400 mm in the measuring tube is needed, and the present pressure exerted by that vapor is 475 mm. Since the float valve cannot be opened under this pressure differential between 475 mm and vacuum, it is necessary to cool the vapor to condense it to diminish the pressure. Then, after the float valve has been opened, the amount of vapor to be allowed to escape from the tube before the valve is closed again can only be determined by trial and error. This will usually require several rather tedious adjustments. A stopcock, however, offers much easier adjustment. In the above example, it would only be necessary to open it very slightly until the pressure dropped exactly to 400 mm. Therefore it is convenient to take advantage of the fact that most vapors will not react with stopcock lubricant, and include in the vacuum line a measuring tube like that shown in Figure 24.

**Volumes above Room Temperature.** It is sometimes convenient to measure, by gas volume, materials of low volatility, for example, below 20 mm at room temperature. To do this, it is necessary to increase the temperature of all parts of the system, including the manometer. An apparatus<sup>4</sup> is shown in Figure 25. It consists of a bulb and a mercury manometer of measured volume, so constructed that the whole assembly can be surrounded by a constant temperature bath. The operation is as follows: The apparatus is thoroughly evacuated, with the mercury in the reservoir. The sample is then condensed in the volume bulb, and cut off from the system by lifting the glass rod to allow mercury to flow up into the manometer under

<sup>3</sup> R. T. Sanderson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 76 (1943).

<sup>4</sup> Slightly modified from that of A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937).

pressure of the atmosphere in the reservoir. If, as originally designed, the apparatus is then heated in a bath, it is necessary to continue to add mercury to the manometer as the pressure rises, to maintain the cut-off and to measure the pressure. In this case, a pressure corresponding to complete vaporization of

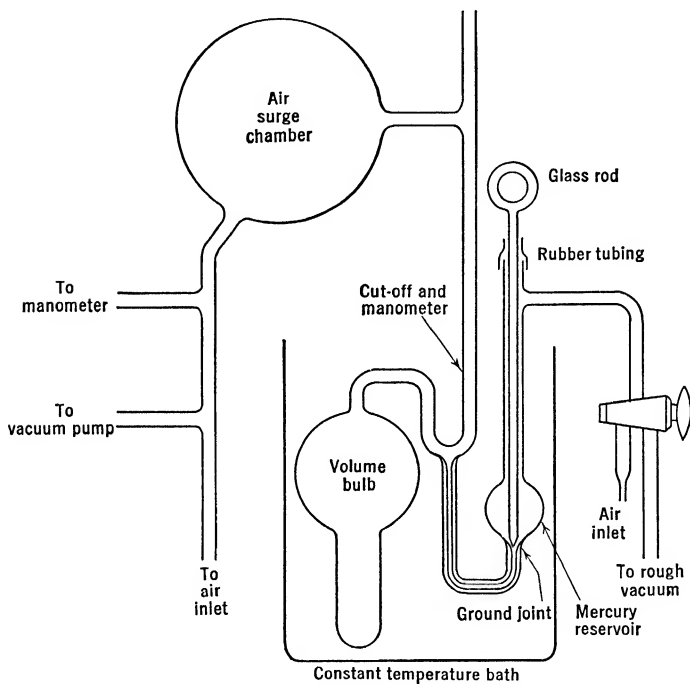


FIG. 25. Apparatus for measuring vapor volume above room temperature.

the sample is measured directly, by using a cathetometer (which is a telescope on a calibrated vertical bar), and, from this and the volume of the bulb and the temperature, the theoretical vapor volume of the sample at room temperature may be calculated.

To avoid the necessity of increasing the amount of mercury in the manometer as the pressure rises, and to avoid also the difficulty in trying to correct the pressure for the thermal gradient in the mercury column which rises partly out of the temperature bath, and to eliminate the necessity of reading the pressure by

means of a cathetometer, the modification shown in Figure 25 may be used. Here the mercury is run into the manometer to a calibrated mark at zero pressure, after the sample is condensed in the bulb. As the bath temperature and consequently the pressure in the bulb rise, the pressure is exactly equalized by admitting air to the opposite side of the manometer from the bulb. A large air chamber is used to permit easier adjustment of pressure. This part of the apparatus is connected with a manometer at room temperature, on which the pressure in the bulb may readily be measured with a meter stick.

In using these methods, it is important to be sure that the sample has been completely vaporized. For this purpose it is desirable to take a series of readings at increasingly higher temperatures.

## *Measuring Vapor Pressure*

No other physical property of volatile materials is more generally useful or more conveniently measured in the high vacuum apparatus than the equilibrium vapor pressure. It is the simplest criterion of purity or homogeneity, and the simplest means of compound identification. It is very useful information pertinent to all procedures for separation of materials by fractionation.

### BELOW ROOM TEMPERATURE

Vapor pressures of materials below room temperature can easily be measured by the static method of enclosing the material in a tube connected to a manometer, cooling the material to the desired temperature, and reading the pressure directly. The calibrated U-tube illustrated in Figure 23 on page 78 is quite satisfactory for such determinations as long as sufficient material is available to provide a condensed phase at the temperature of measurement. When only smaller amounts are available, apparatus of the type shown in Figure 26 is useful.

A convenient method of obtaining the complete vapor pressure curve up to room temperature for a compound is to condense the compound by cooling to a temperature where its vapor pressure is negligible, and then take a succession of readings of pressure and temperature as it warms. For this purpose it is useful to cool a suitable liquid bath to the desired temperature by use of liquid nitrogen, and then to speed the warming-up process between desired temperatures by adding small quantities of the same liquid medium at room temperature to the bath, stirring well to obtain uniformity. In a good Dewar flask, the bath temperature will increase only very slowly on standing. It is well to check this by first reading the temperature, then the pressure,

and then the temperature again. Normally the two temperature readings will be identical, unless the manometer is being read by a very precise method requiring an appreciable amount of time. Unless very precise vapor pressure data are needed, it is satisfactory to measure both temperature and pressure to the nearest 0.2 unit ( $^{\circ}\text{C}$  or mm). With care, the pressure may be measured thus with an ordinary meter stick. More accurate measurements require use of some such device as a telescope mounted on a vertical, calibrated stand (a cathetometer).

### ABOVE ROOM TEMPERATURE

The static measurement of vapor pressures above room temperatures requires apparatus for enclosing the entire vapor space within the temperature bath. Since the vapor space extends to the mercury in the manometer, the manometer must also be included in the bath. Such apparatus is illustrated in Figure 27. It will be noted that this apparatus is practically identical with that illustrated in Figure 25, page 80, which is used for determination of vapor volumes above room temperature, except for the size of the bulb which contains the material under study. The smaller bulb is used here to make the apparatus adaptable to smaller samples and thereby increase the limit of vapor pressure which can be measured.

Operation of this apparatus is likewise very similar to operation of that described on page 81. Mercury is kept entirely in the reservoir until the apparatus is evacuated and the sample condensed in the bulb. Then mercury is permitted to flow up into the U-bend cut-off to a definite mark by loosening the ground-glass joint valve and opening the reservoir to atmospheric pressure. The whole assembly of tube, cut-off, and reservoir is then surrounded by a liquid constant temperature bath, and heating is begun. As the pressure in the bulb increases, the mercury level in the cut-off is kept constant by admitting air to counteract

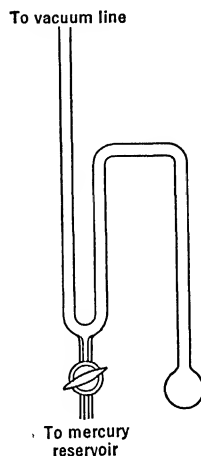


FIG. 26. Apparatus for measuring vapor pressure of small samples.

exactly the pressure in the bulb. When the desired temperature for a reading is reached, only the temperature of the bath and the pressure as read from the manometer which is at room temperature are needed.

Since the vapor pressure of mercury at  $100^{\circ}\text{C}$  is 0.3 mm, and 1 mm at  $126^{\circ}\text{C}$ , small errors are introduced into vapor pressure

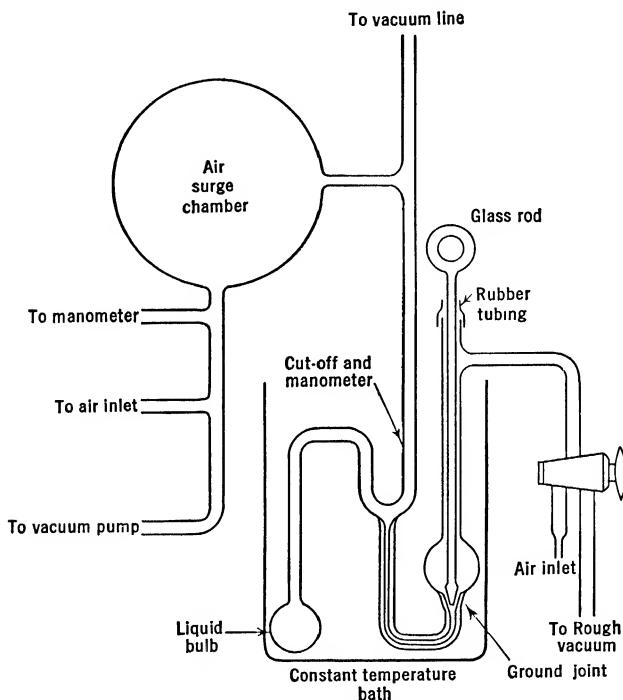


FIG. 27. Apparatus for measuring vapor pressure above room temperature.

measurements by the above method. Mercury distills upward and condenses on the air side, whereas on the vapor side of the cut-off mercury vapor tends to diffuse slowly through the tube. The vapor pressure of mercury at the temperature of measurement would therefore represent the maximum error due to this source, and for most practical purposes it can be neglected at temperatures below  $100^{\circ}\text{C}$ .

Most compounds having vapor pressures of about 1 mm at room temperature have vapor pressures of 60–200 mm at  $100^{\circ}\text{C}$ ,

and compounds with vapor pressures around 20 mm at room temperature usually reach 760 mm approximately in the range 100°–130°C. Thus the above-described apparatus will be found suitable for measuring the vapor pressures of all materials which can be handled in a high vacuum system, at least up to 60 mm, and in many cases up to 760 mm.

Stock<sup>1</sup> has described a simple means of measuring vapor pressures above room temperature, but it requires sealing the apparatus off from the vacuum system.

Brown and coworkers have developed apparatus somewhat similar to that described herein, but affording greater precision of measurement; it is called the *dissociation tensimeter*,<sup>2</sup> which, as the name indicates, is used for measuring dissociation pressures.

## VAPOR PRESSURES OF PURE COMPOUNDS

Reference tables of vapor pressures of pure compounds at easily producible low temperatures are given in the Appendix, pages 117–118, 123–149.

<sup>1</sup> A. Stock and E. Kuss, *Ber.*, **47**, 3115 (1914).

<sup>2</sup> H. C. Brown, M. D. Taylor, and M. Gerstein, *J. Am. Chem. Soc.*, **66**, 431–435 (1944).

## *Condensation Traps and Fractionation*

One of the most important operations in chemical high vacuum work is the separation of compounds of different volatility by fractional distillation-condensation. If a mixture is condensed and then allowed to warm to a temperature at which only one component has an appreciable vapor pressure and the volatility of the other components is still negligible, it should be possible to distill that component quantitatively away from the mixture. This may be thought of as fractional distillation in its simplest form. Similarly, if the whole mixture is allowed to flow as a vapor into a trap held at the above temperature, the most volatile component should flow through the trap, leaving the rest of the mixture behind in a condensed phase. This is fractional condensation. For reasons to be given presently, these processes are usually combined in vacuum line separations.

### PRINCIPLES OF CONDENSATION

It is a common error to suppose that a condensable gas may easily be separated quantitatively from a relatively noncondensable gas merely by passing the mixture through a zone having a temperature at which the vapor pressure of the condensable gas is negligible. Actually, such a separation may be far from quantitative. There appear to be at least two possible explanations for this. First, the condensable material may be passing through the trap in such a manner that it does not become cooled to the temperature of the trap. Second, the condensable material may be cooled to the trap temperature but in such a physical



state as to be entrained with the noncondensable gas. These possibilities need further consideration.

According to kinetic theory, a gas diffusing at a moderate pressure differential into an evacuated tube will not travel very far, in terms of the diameter of the tube, before every molecule has collided with the walls of the tube at least once. In part, this is demonstrated by the fact that, when the tube is a trap at a temperature at which the vapor pressure of the gas is negligible, the gas condenses quantitatively in a narrow ring at the nearest part of the cold zone. If the gas were not condensable at the temperature of the trap, the path of molecules moving toward the walls would be obstructed to a much greater degree by molecules bouncing from the walls, so that the gas would go somewhat farther into the trap before every molecule would have struck the wall at least once. Even then, however, the distance into the trap would not be very far. When the gas is passing through the trap at low pressure, the probability seems great that every molecule will strike the trap walls many times. Therefore it seems quite unlikely that incomplete fractional condensation would be caused by incomplete cooling of the gas in the trap. Rather, it appears that imperfect functioning of a condensation trap would be due to some form of entrainment of the condensable material by the noncondensable gas.

It is easy to imagine such entrainment by considering the mechanism by which a gas in a trap is cooled. If all the molecules of the gas are condensable, practically all collisions with the cold walls of the trap will presumably be inelastic, so that the gas coats the walls of the trap in a condensed phase. Thus it would be essential for a molecule to strike the trap wall before losing its thermal energy. If, however, part of the molecules are of a compound which is not condensable at trap temperature, these molecules may be cooled by a wall collision and then, rebounding, may in turn cool molecules of condensable material which are in the intrawall space. Instead of building up crystals on the walls, some of the condensable molecules may then form solid aggregates in space. These solid particles, although they have no appreciable vapor pressure, may be small enough to be carried out of the trap by the stream of noncondensable gas. In addition, it is conceivable that combination of these tiny

aggregates to form heavier crystals, which would settle out of the gas stream more readily, may in some cases be inhibited by adsorption of a layer of the noncondensable gas on the surface of the aggregates. Building up of crystals on the trap walls might similarly be inhibited. It seems, then, that both the traps and the fractionation procedures should be designed to minimize entrainment.

### DESIGN OF TRAPS

A condensation trap in a vacuum system is simply a tube through which gases may be made to flow, and which may be

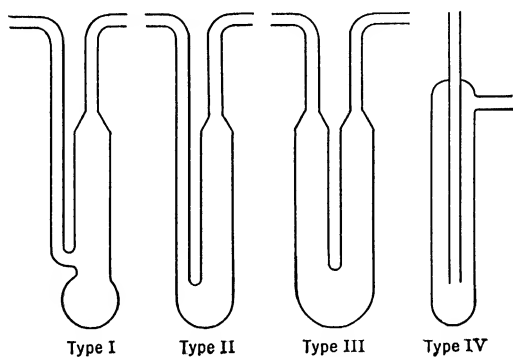


FIG. 28. Condensation traps.

immersed in a cooling bath. In order to attain greatest efficiency, traps should be designed, according to the above discussion, for lowest possible gas velocity and a minimum of turbulence. This means wide bore tubes with a minimum of sharp bends or constrictions. Condensation traps which are designed to provide very thorough cooling, such as helical traps of narrow tubing, are actually less efficient for separating condensable from noncondensable materials than are ordinary wide bore U-tube traps.

Four types of traps are illustrated in Figure 28. Type IV is very commonly used, and it is suitable for such a purpose as protecting a pump against vapors in an ordinary laboratory vacuum distillation. However, it is not recommended for high vacuum work because it cannot be heated adequately to desorb gases. The surfaces of the inner tube are not accessible to direct

heating, and the ring seal should not be strongly heated because of the possibility of breakage. Traps of Type I are useful when a considerable amount of liquid condensate, coming from the wide side only, is expected. Type II traps are designed for use where vapors approach from only one side. For example, they are often used as a final trap between the vacuum line and the pump. Type III traps are ordinary U-tubes and are of very general utility.

In a high vacuum apparatus, these traps are repeatedly subjected to large and rapid temperature changes. To minimize the resultant thermal strains, the glass should be as thin as possible, adequate mechanical strength being maintained. The large bore sections of the traps illustrated may be constructed of test tubes, which have thinner walls than standard tubing of the same diameter. Annealing of such traps is also very important.

## FRACTIONATION PROCEDURES

Separations in a high vacuum system are usually carried out by a combination of fractional distillation and condensation through a series of simple traps. Such a series, as shown in Figure 29, consists merely of a number of U-tubes connected in series by mercury float valves. Since these traps serve also as receivers of the various fractions, each is independently and directly connected also to the main vacuum line through a mercury float valve to facilitate subsequent treatment of the separate fractions.

This fractionation procedure depends on there being sufficient difference in volatility of the individual components of a mixture so that each component will have a vapor pressure of at least  $\frac{1}{2}$  mm when the component of next lowest volatility is cooled to where its vapor pressure is negligible. The word "negligible" is relative. Actually, at low vapor pressures the change of vapor pressure with temperature is relatively slow, giving a fairly large temperature span, for example, between 0.5 mm and 0.01 mm. The problem is almost never the separation of a volatile material from a completely nonvolatile material. Instead, it involves separation of substantially all of the more volatile material in a short enough time so that only a very insignificant amount of

the less volatile material can vaporize. Therefore, time becomes an important element in fractionation of this type. As an illustration, water has a vapor pressure at dry ice temperature ( $-78.5^{\circ}\text{C}$ ) a little below  $10^{-3}$  mm. In a fractionation process of long duration, appreciable quantities of water vapor may come from a trap at that temperature, but the rate of evaporation is so very slow at that low vapor pressure that, in a fractionation requiring only a few minutes, the separation of a more volatile

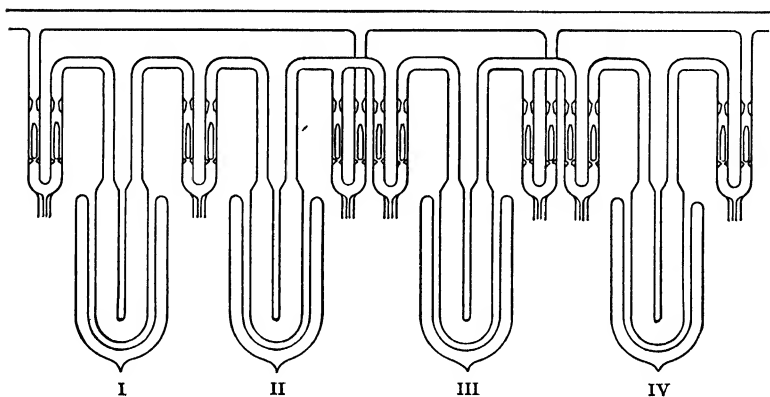


FIG. 29. Fractionation train.

material from water can be made practically quantitative by proper use of dry-ice-cooled traps.<sup>1</sup>

**Binary Mixtures.** The principles of a fractional distillation-condensation procedure may be described by illustrating with a simple binary mixture. Let the components be *A* and *B*, of which *A* is the more volatile. If this mixture were to pass directly, in the vapor state, into a condensation trap cooled to retain *B*, an appreciable part of *B* might be entrained and carried through the trap by *A*. This is why it is usually better to combine distillation with condensation. The mixture of *A* and *B*, contained in the first trap (I) of the series, is first cooled to a very low temperature at which the vapor pressure of *A* is negligible. Mercury in the float valve between traps I and II is

<sup>1</sup> For calculation of the rate of evaporation of solids in high vacuum, see I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221–2295 (1916).

adjusted to a height at which the valve may be used as a manometer. The mixture is warmed to a temperature at which a vapor pressure of about 1 or 2 mm is shown. Trap II is then cooled to that same temperature, and trap III is cooled to a lower temperature at which the vapor pressure of *A* is practically zero. The valves between the traps are now opened. In a very few minutes most of *A* will distill over through trap II and condense in trap III, leaving substantially all of *B* in trap I. Some of *A* may still be contained in *B*, either mechanically entrained or in liquid or solid solution. Trap I is therefore now allowed to warm slowly. *B* will slowly evaporate and be condensed in trap II. Remaining traces of *A* will go through trap II without entraining appreciable amounts of *B*. The two components, if sufficient difference in volatility and not too great mutual solubility are assumed, are now substantially quantitatively separated.

A sample of *A* containing even less of *B* may be obtained by repeating the process, starting with the contents of trap III exactly as if it were the original mixture, and then finally distilling the bulk of *A* at a pressure of about 1–2 mm away from any traces of *B*, not allowing *B* to vaporize at all.

A sample of *B* containing even less of *A* may be obtained by repeated evaporation and fractional condensation in a trap at the same temperature as the original trap II.

If the components *A* and *B* are quite soluble in each other, complete separation may require repeating the above procedures several times.

**Polycomponent Mixtures.** A polycomponent mixture may often be fairly well separated into its individual components by fractional condensation through a series of traps cooled to successively lower temperatures. For example, a mixture of hydrogen, carbon dioxide, and water vapor could be separated roughly by allowing it to diffuse slowly into a series of two traps cooled to  $-78.5^{\circ}\text{C}$  (dry ice) and  $-196^{\circ}\text{C}$  (liquid nitrogen) respectively. Practically all the water vapor would be trapped in the first and all the carbon dioxide in the second, with the hydrogen passing through both. However, it is often more convenient, and practically essential with mixtures of unknowns, to treat polycomponent mixtures as successive binary mixtures, separating the

most volatile component each time as a pure compound. Thus, an unknown mixture may be treated exactly like the binary mixture of *A* and *B*, with *A* the more volatile component. When separation of *A* appears complete, *B* is treated as a binary mixture, and so on.

**Criterion of Purity.** In fractionation of the type described above, it is necessary to be able to determine whether or not a given fraction is pure—homogeneous with respect to volatility. Reproducibility of vapor pressure is a property of pure compounds which can easily be measured in the high vacuum system.

The simplest test of a fraction is to bring it into a tube connected with a manometer and measure its vapor pressure when it has been both warmed and cooled to the same temperature. Whether a pure compound is condensed to zero vapor pressure by liquid nitrogen and then warmed rapidly to dry ice temperature, or merely cooled rapidly from room temperature to dry ice temperature, it will reach the same vapor pressure promptly. If it contains impurities of different volatility, however, attainment of vapor pressure equilibrium will be slowed greatly. For example, the presence of a small amount of a more volatile impurity will impede diffusion of the vapor of the major component toward the cold zone to such an extent that the equilibrium vapor pressure will be reached only slowly.

The best method of applying this principle of constant or reproducible vapor pressure is to fractionate the fraction by distillation at a pressure of about 1 mm and then determine whether the separate portions are identical in vapor pressures over a wide temperature range. For greater sensitivity it is preferable to measure vapor pressures up to several hundred millimeters, if sufficient material is available. If the fraction is a pure compound, all portions will have identical properties. If it is not pure, the more volatile component will be concentrated in the part distilled away at 1 mm pressure, so that this part will exert somewhat higher vapor pressure than the residual part.

Although all volatile pure compounds will, of course, pass this test, homogeneity of a fraction with respect to volatility is not entirely conclusive evidence that the fraction is a pure compound. Mixtures of close boiling isomers, for example, would appear to

be fairly pure compounds by this test. Therefore, other criteria must be applied to establish chemical individuality of a fraction. The vapor pressure test gives information about the effectiveness of the fractionation procedure.

Fractional distillation-condensation in traps is best suited for quantities ranging from about 1 ml of vapor to several milliliters of liquid. When larger amounts are available and when closer fractionations are required, use of conventional types of distillation columns is recommended.<sup>2</sup> Further development in this field is much to be desired.

### COMPLETENESS OF CONDENSATION

The following example is given to illustrate the magnitude of error to be expected if condensation is not permitted time for completion. If a sample is being condensed in a tube connected to a vacuum system with a total volume of 5 liters, a pressure of  $10^{-3}$  mm due to uncondensed material represents less than 0.01 ml at standard temperature and pressure.

<sup>2</sup> See, for example, A. B. Burg, *J. Am. Chem. Soc.*, **56**, 499-501 (1934).

## *Miscellaneous Suggestions and Methods*

### MOLECULAR WEIGHTS AND VAPOR DENSITIES

The essential steps for the most obvious method of determining the molecular weight of a volatile compound, or the average molecular weight of a mixture, have already been described in detail. They are, simply, to measure the vapor volume and also the weight. On the basis of Avogadro's Hypothesis, the molecular weight is equal to 22,412 times the sample weight in grams divided by the sample volume in milliliters at standard conditions.

Another method of determining the gas or vapor density, and hence the molecular weight, makes use of the acrostatic or floating balance. A simple form of this<sup>1</sup> is shown in Figure 30. It consists of a light glass balance contained in a tube which is attached to the vacuum line. The balance consists of a thin glass rod, with a sealed sphere about 1.5 cm in diameter at one end, and a solid counterweight, terminating in a fine pointer, at the other end. At the middle point of the rod, two tiny feet, terminating in needle points, are attached. These feet rest in two small saucers, so that the balance is free to oscillate with very little friction. The pointer moves over a scale or a fixed point, its position being read by means of a magnifying glass, if desired. A tube containing a small thermometer, a small condensing chamber, and a short mercury manometer are attached to the tube containing the balance.

<sup>1</sup> A. Stock and W. Siecke, *Ber.*, **57**, 562 (1924).



The lifting force on the small bulb depends on the density of the gas. If the balance is calibrated by use of air or other suitable gas such as carbon dioxide, so that at a given pressure the pointer is at a determined position, any other gas of the same density will move the pointer to that identical position. The pressures of the two gases will be to each other inversely as their normal densities when the pressures are compared on the basis of equal temperatures.

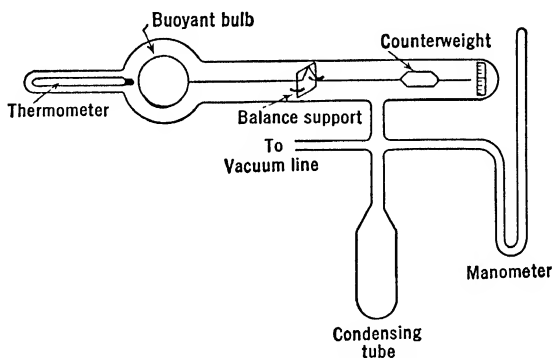


FIG. 30. Aerostatic gas density balance.

It is claimed that this device permits rapid and accurate determination of gas density of samples as small as 1 ml. It seems certainly more convenient than methods requiring removal of the gas sample from the vacuum line for weighing.<sup>2</sup>

## DETERMINING MELTING POINT

Melting points of materials may be determined in the high vacuum apparatus by means of the apparatus shown in Figure

<sup>2</sup> The aerostatic balance has been developed to a more precise and sensitive instrument, as described by A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N. Y., 1933, pp. 186–189, who lists therein references to the original literature. Further details of construction and operation are also to be found in *Experimental Methods in Gas Reactions* by A. Farkas and H. W. Melville, Macmillan and Co., Ltd., London, 1939, pp. 299–301.

31.<sup>3</sup> It consists of a thin-walled, vertical tube containing a thin glass rod terminating in a cross at the bottom and a pointer at the top, and having a sealed-in iron core at the center. This rod may be lifted by means of a magnet applied outside the tube. While it is held thus suspended, the material whose

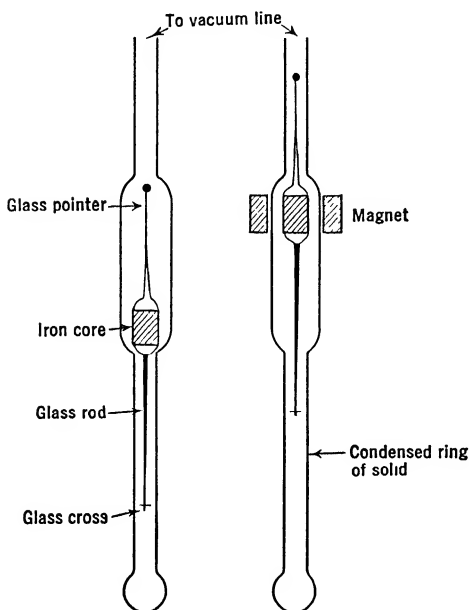


FIG. 31. Melting point apparatus.

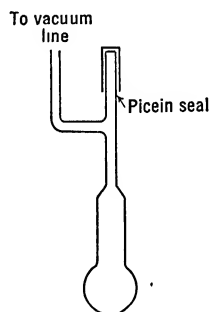


FIG. 32. Tube for drying ammonia.

melting point is to be determined is condensed by use of liquid nitrogen to form a solid ring near the bottom of the tube and below the end of the rod. The rod is now lowered so that the cross rests on the solid ring. The magnet is removed. The liquid nitrogen bath is now replaced by a cooling bath which is allowed to warm very slowly, with the bulb of a vapor pressure thermometer directly beside the solid ring in the tube. The glass pointer, which can be observed above the cooling bath, is watched. The temperature of the bath at precisely the moment

<sup>3</sup> A. Stock, *Ber.*, **50**, 156 (1917).

when the rod begins to fall corresponds to the melting point of the compound in the tube, within, it is claimed,  $0.1^{\circ}\text{C}$ .

### REACTIONS AT PRESSURES GREATER THAN 1 ATMOSPHERE

All such reactions should be carried out apart from the high vacuum line, which, however, may very conveniently be used to measure and introduce volatile materials into a bomb tube and, later, to separate and analyze the products. Well-annealed, heavy-walled tubes of small diameter (1 inch or less) may be used fairly successfully for pressures up to 150 lb per sq in., although the use of glass for such pressures is very dangerous unless complete precautions against explosion are taken. The operator should never expose himself to a glass tube under pressure, but should wait until it is cool enough for the pressure to be normal. If the room temperature pressure is still above atmospheric, provision should be made for cooling below room temperature by remote control.

### DRYING LIQUID AMMONIA

On a small scale, for conducting experiments using liquid ammonia in the vacuum apparatus, the ammonia may be dried within the apparatus. Ordinary commercial ammonia, or ammonia evolved from its salts by the action of strong alkali, is condensed in a tube of the type shown in Figure 32. While the ammonia is condensed, nitrogen is admitted to the apparatus to 1 atmosphere pressure. The cap is then removed from the top of the tube, and a small piece of sodium metal is dropped in. The cap is replaced, sealed with picein, and the nitrogen is pumped out of the system. The float valve between tube and vacuum line is closed, and the ammonia is allowed to warm to about  $-75^{\circ}\text{C}$ , just a few degrees above its melting point. The sodium dissolves very readily, forming a beautiful deep blue solution, or a bronze solution if more concentrated. Any water in the ammonia is decomposed rapidly, liberating hydrogen. On longer standing, appreciable amounts of hydrogen are also formed by reaction of the sodium with the ammonia, giving sodium

amide, but the rate of amide formation is very slow at the low temperature. The liquid ammonia is then frozen again at a temperature at which its vapor pressure is negligible, and the evolved hydrogen is pumped away. Anhydrous ammonia may now be distilled from this tube and condensed wherever needed in the vacuum system.

### PREPARATION OF WEIGHED SAMPLES OF SODIUM

The high vacuum line is a convenient place to study, on a small scale, reactions of sodium metal. One method of preparing small weighed samples of sodium for such studies follows. A small amount of sodium is melted in a test tube. One end of a clean, dry glass tube about 4 mm in diameter is put beneath the oxidized surface of the molten sodium, and the sodium is drawn up into the tube by use of vacuum applied to the other end. This must be done rather quickly, since the sodium solidifies in the tube. This tube serves as the sodium supply.

A number of tubes of the type shown in Figure 33 are prepared, with one end drawn out to a capillary in the end of which a small bulb is blown. Such a bulb about 4 mm in diameter will hold roughly 20–40 mg of sodium. Each tube is carefully weighed. Then the tubing containing the sodium is broken into pieces about 1 cm long, and one piece is quickly placed in each of the tubes, which are promptly sealed with picein to a manifold, as shown in Figure 33. The manifold and tubes are then thoroughly evacuated. Next, one at a time, the tubes are heated in a test tube oil bath hot enough to melt the sodium (m.  $97.6^{\circ}\text{C}$ ). The melted sodium runs from the tubing but usually remains as a globule at the top of the capillary, as in C, without running down into the tiny bulb. The oxide will either remain in the tubing or float on this globule. If the sodium does not run into the bulb, it is necessary to admit just enough nitrogen pressure to force the sodium through the capillary to fill the bulb. Then the nitrogen is pumped away and the oil bath removed. Next, the capillary, which will also contain sodium, is very carefully heated with a small flame to distill the sodium out of it back to the upper part of the tube. When this has been accomplished

(*E*), the capillary is melted and the bulb sealed off from the system, as in *F*.

When all the bulbs have been filled with sodium and sealed off in this manner, air is admitted to the manifold, and the residual tubes are unsealed, cleaned of sodium and picein, and

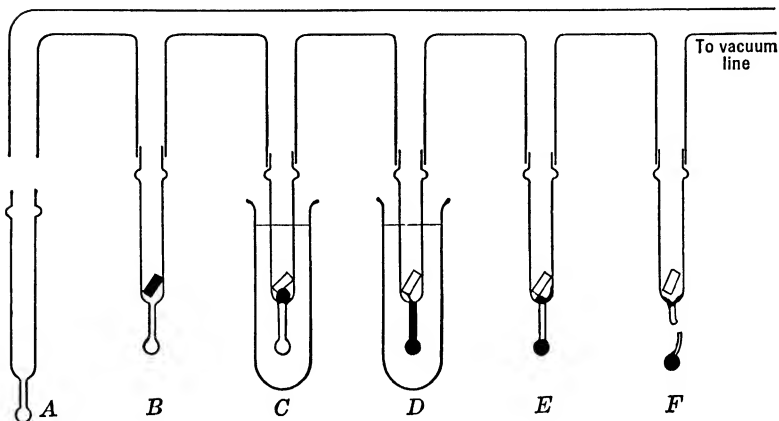


FIG. 33. Apparatus and successive steps in preparing weighed samples of sodium.

weighed individually with the corresponding bulb of sodium. The weight gain is thus the weight of the sodium.

### INTRODUCING WEIGHED SODIUM TO THE VACUUM LINE

A method of introducing a weighed sample of sodium to a reaction tube in the vacuum system makes use of a bulb-crushing device such as that shown in Figure 34. The reaction tube is fitted with a side arm, as shown in Figure 35, large enough to admit the bulb-crushing device, and sealed shut at the end. The other reactants, or solvents such as ammonia, may be condensed in the reaction tube either before or after the sodium is admitted. If before, they are kept frozen at a temperature corresponding to a negligible vapor pressure during the introduction of the sodium. The reaction tube is filled with nitrogen to a pressure slightly in excess of atmospheric. The end of the side arm is then

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broken off, and a slow nitrogen stream is passed through the system and out at this point, to prevent air or moisture from getting in. The bulb containing the sodium sample is held in

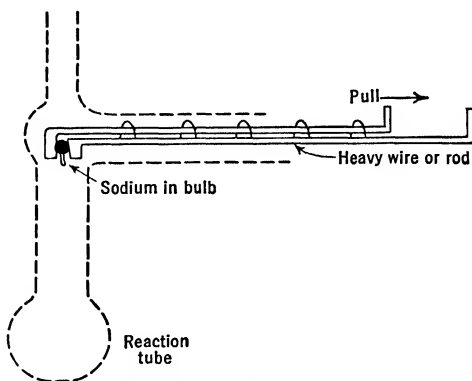


FIG. 34. Bulb crusher.

the bulb crusher and inserted in the side arm until it is directly over the main reaction tube. It is then crushed and allowed to drop into the tube. The bulb crusher is removed, and the side arm is heated and drawn down to a capillary while nitrogen is still being passed through it. Then the nitrogen supply is shut off and the capillary is sealed off, and the end of the side arm is pulled away. In this manner, entrance of air or moisture during the sealing-off process can be avoided.

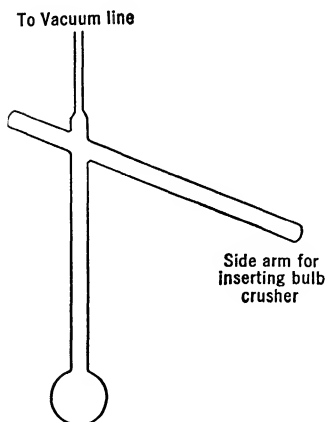


FIG. 35. Reaction tube for sodium.

Nitrogen is now pumped away, and the reaction is allowed to proceed.

If it is desired, hydrogen may be used in place of nitrogen. In this case, however, it is well to ignite the hydrogen stream coming from the open side arm just before beginning to seal off this arm. When the capillary has been formed, the hydrogen source may then be turned off and

the seal completed before the flame can work its way up the side arm.

A method of exposing a large surface of the sodium to the action of other materials is to condense enough ammonia in the reaction tube to dissolve the sodium from the crushed bulb, keeping the temperature at about  $-75^{\circ}\text{C}$ . The ammonia may then be distilled away from the sodium at this temperature, leaving the metal in a form better exposed for subsequent reaction. A modification is to include, in the bottom of the reaction tube, a small piece of glass wool on which the sodium can be deposited when the ammonia is evaporated.

### HYDROLYSIS OF METAL HYDRIDES AND ORGANOMETALLIC COMPOUNDS

Reactions such as hydrolysis of metal hydrides, which produce nonvolatile materials, are best carried out in tubes separate from the high vacuum apparatus. The ordinary storage tubes described on page 66, with side arms having capillary tips for use with the tube opener, are satisfactory. A measured sample of the material to be hydrolyzed is first condensed in the storage or "bomb" tube, which is attached to the system with picein. Next, an excess of water is condensed in the same tube, the temperature being kept low with liquid nitrogen. The tube is then sealed off from the line and allowed to warm to the desired reaction temperature. Obviously, the tube should be large enough with respect to the sample to hold the hydrogen or other gas liberated by hydrolysis without undue pressure.

After hydrolysis is considered to be complete, the tube is cooled with liquid nitrogen and opened into the line through the tube opener. The noncondensable gas is pumped into the gasometer by means of the Töpler pump, and any other volatile products of the hydrolysis are separated from the excess water by fractionation. The nonvolatile material may then be removed in the tube for analysis.

### OXIDATION

For analytical and other purposes it is sometimes convenient to be able to bring about the oxidation of volatile materials with

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oxygen within the vacuum line. For example, examination of the oxidation products would serve as a means of identifying noncondensable gases such as hydrogen and carbon monoxide, or as a means of analyzing mixtures of hydrogen and methane.

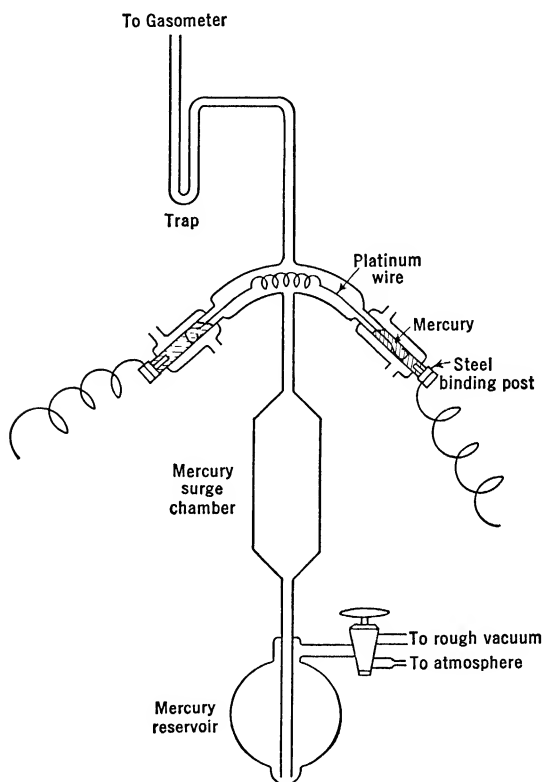


FIG. 36. Apparatus for direct oxidation over platinum.

Suitable apparatus is shown in Figure 36. It consists of an oxidation chamber containing a coil of platinum wire which may be heated electrically, and a mercury surge chamber for circulating gases over the platinum.

The combustion chamber is so designed that the platinum wire may very easily be installed or replaced. The platinum is simply an unattached piece of wire, coiled at the center to provide a concentration of heat, and coiled slightly at each end to fit the



tubing, and to support it in the proper position. Electrical contact is made through mercury which in turn surrounds one end of steel binding posts which are sealed into the side tubes with wax. Small water jackets are provided to keep the mercury and the wax cool. Initially, after the platinum wire is inserted, the binding posts are sealed in place, and the apparatus is evacuated. Mercury is then forced upward from the reservoir in sufficient quantity to run over into the side arms enough to form a contact between the ends of the platinum wire and the binding posts. If it should become necessary to replace the platinum, air is admitted, the picein is softened, and the binding posts are removed to allow the mercury to drain out. The wire is then easily replaced, and the combustion chamber is made ready for operation as before.

Oxidation is carried out as follows. The sample, not over 5 ml of gas, which is to be oxidized is condensed in the small U-tube trap if possible. If it is noncondensable, it is forced directly into the oxidation apparatus from the top of the gasometer. A large excess of oxygen, measured in the gasometer if desired, is then forced into the apparatus. When the oxygen and other material are mixed, the platinum is heated so that the coil glows almost white hot. The mixed gases are circulated over the platinum by repeatedly filling and emptying the mercury surge chamber. When oxidation is believed to be complete, the gases are pumped into the gasometer again through a trap cooled with liquid nitrogen. The carbon dioxide, if any, can be separated from the water and identified by vapor pressures and measured. Water can be determined in various ways, for example by condensing it in a tube containing lithium hydride and measuring the evolved hydrogen.

## C H A P T E R      T H I R T E E N

### *Practice in High Vacuum Technique*

Some preliminary training and experience with the simplest form of high vacuum apparatus should be very helpful to the beginner, before an attempt is made to construct and operate complete equipment for research. The purpose of this chapter is to suggest one of many possible methods of becoming familiar with high vacuum technique. This method involves constructing apparatus containing only the minimum essentials and using it to learn by practice some of the most common and useful operations. Familiarity with information given in the preceding chapters is, of course, a prerequisite to beginning this work.

An irreducible minimum of parts of a general purpose high vacuum apparatus would include the following:

- (1) Mechanical pump and mercury diffusion pump.
- (2) Apparatus support.
- (3) Main line, separated from pumps by condensation trap.
- (4) McLeod gage.
- (5) Calibrated volume tube and manometer.
- (6) Series of condensation traps.
- (7) Tube opener.
- (8) Opening for attaching external apparatus.
- (9) Dry air inlet.
- (10) Stopcocks (or float valves) for interconnecting the above apparatus.

Such an assembly is illustrated in Figure 37. A procedure for its construction could be as follows. The individual parts, namely, the four U-tube traps, the manometer, the McLeod gage, the tube opener, and the air-drying tube, are first constructed separately. The ring seal of the McLeod gage may be avoided if desired by modifying the design as shown in Figure 38. Then

an apparatus stand is assembled, and, since it is not intended for permanence, several ring stands with alternately opposing bases may be clamped together with iron cross bars at top and bottom to form a fairly rigid and satisfactory support. The main line, a piece of 20–25 mm tubing, is then clamped in place, and

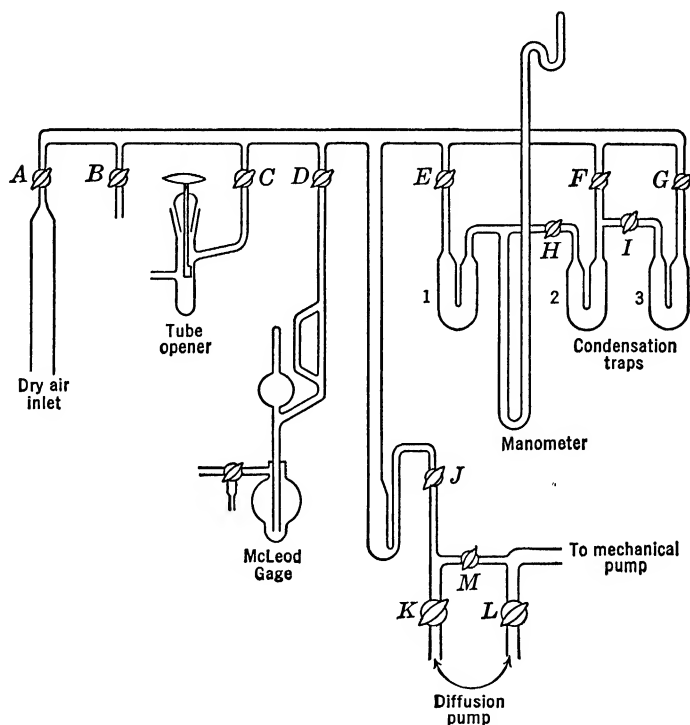


FIG. 37. Simplified form of high vacuum apparatus.

the line to the pumping system and the various other parts of the apparatus are sealed on with stopcocks as indicated. Stopcocks are suggested for use here instead of float valves, for their greater simplicity of assembly and operation. Tubing of about 8 mm diameter is satisfactory for joining the parts to the main line.

When the apparatus has been assembled, the next step is to evacuate it. The mechanical pump may be used directly, without the diffusion pump, for evacuating sufficiently for testing

for leaks with the Tesla coil. After any leaks have been found and repaired and retested, it is then time to begin operating the diffusion pump with the mechanical pump to attain the highest possible vacuum. It will be necessary to bake out the apparatus,

by heating with a flame, as thoroughly as is possible without heating any of the stopcocks. A vacuum of at least as low a pressure as  $10^{-3}$  mm should be attained, without any detectable leaks being present, before any further work should be attempted.

Next, the manometer must be filled with mercury. When this has been done, the apparatus is ready for experimental handling of volatile materials, except that the U-tube attached to the manometer has yet to be calibrated. The following experiment is suggested as a means of calibrating this U-tube while making use of several common procedures in high vacuum technique.

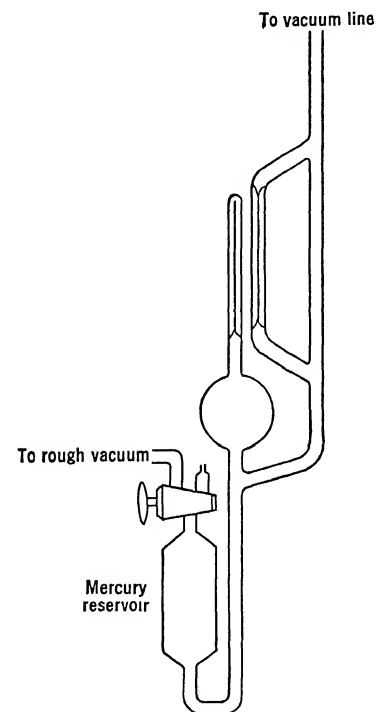


FIG. 38. McLeod gage with modified mercury reservoir.

with picein, to the apparatus at *B* in Figure 37. Then stopcock *B* is opened, the tube is evacuated, and the picein seal is tested for leaks. When a good vacuum has been attained in the system (stopcock *B* may have to be closed temporarily), the apparatus is closed to the pumps at *J*. Then, with *B* and *E* open and all other stopcocks closed, the sodium bicarbonate is carefully heated to cause the reaction



The carbon dioxide and water vapor thus evolved diffuse through the apparatus.

When the bicarbonate has been heated enough to cause a pressure of about 100–200 mm, heating is stopped, and traps 3 and 2 are cooled with dry ice and nitrogen, respectively. When stopcocks *I* and *G* are opened, a fractional condensation occurs, with most of the carbon dioxide diffusing through trap 3 into trap 2, and most of the water vapor freezing out in trap 3. When the pressure in the apparatus is down nearly to zero, stopcock *I* is closed, and *J* is opened, to pump the last traces of carbon dioxide and water vapor from the line, and especially from trap 1. Warming the apparatus with a flame will be found very helpful in speeding the removal of the water vapor.

Next, stopcock *E* is closed, and the carbon dioxide in trap 2 is freed of any entrained water by warming trap 2 just to dry ice temperature, with *H* open and trap 1 cooled with liquid nitrogen. When the transfer of carbon dioxide to trap 1 is complete, stopcock *H* is closed, and the contents of trap 1 are allowed to come to room temperature. Meanwhile, traps 2 and 3 are opened to the pump. *B* is, of course, closed as soon as the contents of the tube are cool, and the tube is removed from the line.

The pressure in trap 1 should now be of the order of a few hundred millimeters, which should be due to substantially pure carbon dioxide. It will now be instructive, first, to establish the homogeneity of this gas with respect to volatility, second, to calibrate the U-tube-manometer assembly by measuring and weighing at least two different size samples of the gas, and, third, to practice removing samples by sealing them off in tubes, and then returning them via the tube opener to the system for remeasuring.

To test the homogeneity of the material, first prepare a cooling bath of carbon disulfide slush. Then place this bath about the trap so that the bottom of the trap is immersed in the slush. (There is no need for immersing an entire trap in a cooling bath unless the trap is to be used as a part of a fractionation train. Enough of the trap should be in the bath to contain all the condensed trap contents.) Notice how rapidly the pressure drops, and read the pressure as soon as it appears to have reached its minimum. Let stand for a few minutes and read the pressure

again to be sure that the first minimum was correct. Then replace the carbon disulfide bath by a liquid nitrogen bath. When the pressure has dropped to zero, remove the liquid nitrogen, and replace the carbon disulfide bath. Notice how rapidly the pressure rises, and whether it reaches the same value as before. The vapor pressure of carbon dioxide at the temperature ( $-111.8^{\circ}\text{C}$ ) of the carbon disulfide slush is 26 mm. If the material is quite homogeneous, the same pressure will be reached rapidly from either direction.

Next, cool the trap with liquid nitrogen, and let warm slowly. When the pressure is about 1 mm, cool adjacent trap 2 with liquid nitrogen and open stopcock *H* between. Allow distillation to take place for a short time, and then close the stopcock. About half to two-thirds of the carbon dioxide sample should be distilled thus into adjacent trap 2, as determined by the pressure at room temperature in the original trap. Any more volatile material has thus been concentrated in the second trap, and any less volatile material will remain in the first. Cool the first trap with the carbon disulfide bath, and read the vapor pressure. It should read the same as for the original larger sample. This determination of homogeneity with respect to volatility merely provides practice in going through the motions; there is little reason to suspect that the carbon dioxide might not be substantially pure.

The sample left in the first trap may now be of suitable size for use in calibrating the trap-manometer system. Read its pressure at the temperature of the room carefully, and estimate roughly the volume at standard conditions. Choose a weigh bulb of slightly larger volume, attach it at *B*, and evacuate it carefully. Then cool it with liquid nitrogen and open stopcock *E* to transfer the sample to the weigh bulb. When transfer is complete, close the stopcock of the weigh bulb and stopcock *B*, and unseal the weigh bulb and weigh it at room temperature. Reseal it to the apparatus, and after the necessary evacuation of the system transfer the carbon dioxide back to trap 1 and once more read its pressure at room temperature. This should be exactly the same as the reading before the sample was weighed. From the weight and the molecular weight, calculate the volume at standard conditions. Then, from the pressure in trap 1, calculate

the volume of the trap-manometer system at that pressure. Correct this volume to a zero pressure reading of the manometer by subtracting the extra volume due to the manometer under pressure. Next, measure out a second sample of carbon dioxide, quite different in size from the first, and repeat this procedure. The calculated volumes of the trap at zero pressure should agree within 0.1 ml.

Now seal, with picein, a transfer tube, prepared for the tube opener, to the apparatus at *B*. Measure out a volume of carbon dioxide in trap 1 and transfer it to the transfer tube. Seal the tube off from the line, and then use the tube opener to readmit the contents to the line. Measure the sample in trap 1 again. If proper care was taken with this manipulation, there should be no evidence of loss.

When this practice vacuum line has been constructed and used as, for example, directed above, the operator will have acquired enough experience to undertake the construction and operation of a better and more generally useful apparatus of the kind that will be briefly described in the next chapter.

## CHAPTER FOURTEEN

### *A General Utility High Vacuum Apparatus*

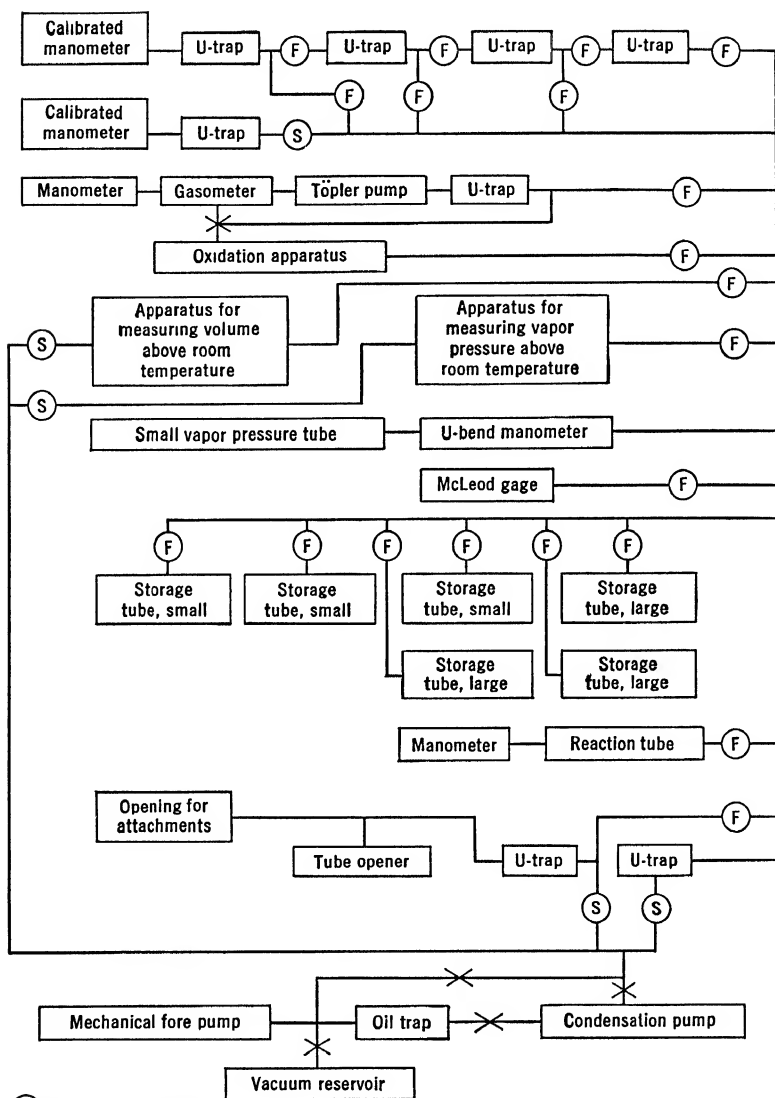
The preceding chapter describes a simplified high vacuum apparatus containing what is somewhat arbitrarily considered an irreducible minimum of parts. For more complete utility, the apparatus can be expanded almost indefinitely to the limits of the available space. It is possible, however, to design a very practical and useful assembly of high vacuum apparatus which is capable of meeting almost all the common requirements of chemical studies of volatile materials, and which occupies a horizontal space of only about 2 by 6 feet. The purpose of this chapter is to describe such a system and to present some suggestions concerning its construction and operation.

It is well to observe the general principle of keeping the apparatus as simple as possible, consistent with the purposes in view. The more involved and complicated the apparatus is, the more difficult it will be to evacuate and keep evacuated, the more difficult it will be to locate leaks, and, in general, the more likely it is that operating troubles will occur. If nevertheless it seems convenient to attach a number of parts which will be used only infrequently, these may be so connected that they may be isolated from the more active part of the apparatus as a unit while they are not in use.

Figure 39 gives a schematic diagram of a general utility apparatus. Since all the component parts and the general principles of their use have been discussed previously, the following suggestions are merely supplementary.

The first necessity, after the component parts have been collected, is a place to assemble them. The apparatus may stand directly on the floor, but it will be much more convenient on a





(F) Mercury float valves

(S) Mercury shielded stopcocks

X Stopcocks

FIG. 39. Schematic diagram of general utility high vacuum apparatus.

bench. The apparatus itself does not need to be more than about 3½ feet high, except perhaps for one or two manometers or the like, and there is very little necessity to handle the upper part. Therefore a good height for the supporting bench would be about 3 feet below the maximum height which the operator can reach easily. The more accessible the entire apparatus is, the better; a separate bench which one can walk all around is ideal. If it is not possible to have such a bench, the apparatus should be approachable from opposite sides, or parts of its construction and operation may prove very awkward. It has been found especially convenient to have a bench enclosed like a cabinet, with a large compartment to contain the pumps and rough vacuum chamber where they will be out of the way, and drawers for keeping the necessary tools and supplementary equipment such as various weighing tubes, and bomb or transfer tubes.

To support the apparatus, alternately faced ring stands clamped together by horizontal iron bars are satisfactory, but a more rigid support can be made from 1-inch pipe upright standards, with welded cross bars at top and bottom to which narrow vertical bars may be clamped where needed. The ideal is absolute rigidity, but this is not essential unless the entire assembly is to be moved frequently and roughly.

When the apparatus support is ready, it is helpful to begin the construction of the glass line by clamping the component parts to the support at approximately their proper places. This enables one to visualize the final appearance and to foresee and forestall spatial difficulties not readily apparent from a drawing on paper.

A compact arrangement will save space, but the necessity for placing Dewar flasks about each of the traps, storage bulbs, and reaction and other measuring bulbs must be kept in mind. It should be possible to move these Dewar flasks into position without tipping them very much, since they will contain liquid coolants. It should also be possible to adjust their position vertically so that the tube may be immersed to exactly the desired position in the bath. This will influence the position of other apparatus clamps, since a clear path should be left for the clamps to support the Dewar flasks. To eliminate much of the otherwise necessary shifting of clamps, ordinary apparatus iron rings, of slightly larger inside diameter than the outside of the Dewar flasks, may

be clamped a few inches below each tube, in a relatively permanent location. The Dewar flasks may then be placed in position by lifting them through the rings until they can be supported on top of the ring by a small square of wood slid under them. The level of the bath about the tube may then be adjusted to some extent by the number of wooden squares placed under the Dewar flask, without changing the position of any clamps.

If all the float valves are to be supplied with mercury from one or two common reservoirs, the reservoirs and the necessary supply lines may effectively be kept out of the way by placing them in approximately the same plane with the apparatus support. The rest of the apparatus may then be mounted about 6 inches away from that support on both sides.

If a vacuum chamber is to be used for operating the float valves and other parts requiring mercury reservoirs, it can perhaps best be made from a steel drum capable of withstanding atmospheric pressure when evacuated. However, a series of glass flasks, each with a capacity not exceeding 5 liters, may be used for this purpose. These should of course be enclosed for protection in case of collapse. Fifteen liters total capacity is suitable for ordinary purposes, but twice that volume is even better. In normal use, such a vacuum chamber needs to be evacuated only once or twice a day to operate the mercury reservoirs, and somewhat oftener perhaps to operate the Töpler pump.

The fractionation train may consist of any desired number of traps, but four are recommended as adequate for most purposes. The trap placed between the pumping system and the vacuum line may always be used as an auxiliary trap for the fractionation train if desired. Incidentally, the importance of this final trap should not be overlooked. It has by far the best location for use in recovering and saving volatile materials which become prevented from condensing in the desired place by accidental leakage of air.

For general purposes, and particularly for convenience in fractionation of multicomponent mixtures, it is convenient to include a number of storage tubes like those shown in Figure 40. An unknown mixture can then be divided roughly into two or three crude fractions, and all but one of these may be stored for later study while one is being further fractionated. Also, it is often

desirable to have ready supplies of certain volatile reagents, such as HCl and  $\text{NH}_3$ , which may be kept on hand in such storage tubes.

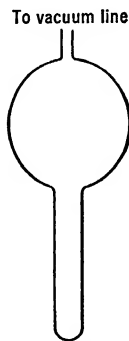


FIG. 40. Storage tube.

The emphasis in this book has been placed chiefly on ways of handling, in the absence of ground joint lubricant, very small amounts of material, that is, from a fraction of a milliliter of vapor to a few milliliters of liquid. There is no basic reason, however, why the same principles and methods may not be adapted to studies of relatively large amounts of material, up to perhaps 50–100 ml or more of liquid. Especially when the use of ground joint lubricant is not undesirable, very versatile assemblies of apparatus may be devised for all types of reactions, both inorganic and organic, except those involving high pressures; ordinary types of equipment with ground glass connections for attaching to the vacuum system, and with stopcocks in place of float valves, may be used. The advantages of this over ordinary techniques are due to the elimination of air and to the quantitative containment of the reactants and products, regardless of how small the quantities may be. The design of the apparatus will therefore be dependent on its intended purpose, and it will be recognized that the general utility high vacuum apparatus represented by Figure 39 is intended as a suggestion of only one of many possible applications of the information given in this book.

## *Future Developments*

In its present state of development, the high vacuum technique for studying volatile compounds is extremely useful. It should by no means be inferred from this that the technique approaches perfection. One of the advantages to be derived from wider use of these methods is that more ideas for improvement will be stimulated and developed. It therefore seems appropriate to conclude this introduction to the applications of high vacuum in chemistry with a brief discussion of some possible future developments.

(1) Although countless formulas for compounding ground joint lubricants have already been developed, there is still real need for a superior lubricant more nearly approaching in properties that described on page 9.

(2) Considerable thought and effort have been devoted to the design of greaseless valves, but there is still ample room for improvement. A greaseless valve is needed which is made of glass and which is very simple in both construction and operation. It should be completely adjustable through all degrees of opening, and when wide open gas diffusion through it should not be impeded. It should operate easily regardless of pressure differential.

(3) Thermometric devices having the simplicity of design of an ordinary liquid-in-glass thermometer, but having greater accuracy and versatility, would be very useful in high vacuum work.

(4) Present methods of separation of materials of different volatility, particularly when only small amounts of vapor are available, are crude, inefficient, and tedious. New methods approaching at least 100 plate efficiency and applicable to very small quantities would be extremely valuable.

(5) It would be useful to have in the main vacuum line a simple, direct, and continuously reading manometer, which would be completely independent of the composition of vapor. It would then be possible to note at a glance the degree of completeness of any transfer of volatile material down to very low pressures.

(6) There is room for improvement of stirring devices capable of simple and efficient operation within a high vacuum system.

(7) With present-day technical knowledge of refrigeration, it would seem possible to design small refrigeration units capable either of replacing many of the conventional cold baths used for cooling traps, or of cooling the cold bath medium prior to placing it in Dewar flasks. One can imagine, for example, meeting the need for a cooling medium at  $-57^{\circ}\text{C}$  by placing a suitable liquid medium in a container in the refrigeration unit, adjusting the unit for the desired temperature, and turning a switch. In a few minutes, without requiring attention, the bath would be ready for use.

(8) If some means of maintaining a high vacuum apparatus wholly at a temperature higher than that of the room could be developed, it would be possible to handle by this technique many compounds now thought of as insufficiently volatile.

(9) Mercury is indeed a unique material which would be very difficult to replace, but a chemically inert, non-solvent liquid of lower density than mercury would be useful, especially in manometers.

(10) Likewise it is difficult to imagine a material as useful for construction of apparatus as glass. Nevertheless a material having the good properties of glass, combined with much greater strength and with a greater flexibility, would not be impossible, and it would certainly be useful in the high vacuum apparatus. Even greater inertness to reactive chemicals would also be a real advantage.

It is indeed fortunate that the practical application of high vacuum technique to the study of volatile compounds does not need to await all imaginable improvements. The methods already available are good enough to be extremely useful in chemical research. For new workers in this field, however, it should be encouraging and stimulating to realize that the problems have by no means been finally solved, that many improvements are still to be made.

## Appendix

Tables VII–XV, inclusive, are taken chiefly from data of Henning and Stock<sup>1</sup> and are to be used with vapor pressure thermometers of the type described on page 57.

Table XVI gives data for use in measuring temperatures between 0° and –192°C with copper-constantan thermocouples.<sup>2</sup>

Table XVII is a collection of melting point, boiling point, and vapor pressure data for pure compounds. The vapor pressures, in millimeters of mercury, are given, for convenience, at temperatures which can easily be produced by cooling baths, as follows:

CS <sub>2</sub> at its melting point	–111.8°C
CO <sub>2</sub> at its sublimation point	–78.5 *
NH <sub>3</sub> at its boiling point	–33.4
H <sub>2</sub> O at its melting point	0.0
Tap water adjusted to	20.0

\* See page 52 for information on reproducibility.

These data were obtained by graphical interpolation on semi-logarithmic paper of vapor pressure data available in the literature. The chief source was the comprehensive compilation reported by Stull.<sup>3</sup> This was supplemented by additional data on organometallic compounds,<sup>4</sup> on boron hydride derivatives,<sup>5</sup> on other hydrides and their organic derivatives,<sup>6</sup> and on miscellaneous commercial organic compounds.<sup>7</sup>

<sup>1</sup> F. Henning and A. Stock, *Z. Physik*, **4**, 227 (1921); A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions*, Macmillan and Co., Ltd., London, 1939, pp. 106–111.

<sup>2</sup> R. B. Scott, in *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, pp. 210–211.

<sup>3</sup> D. R. Stull, *Ind. Eng. Chem.*, **39**, 517–550 (1947).

<sup>4</sup> C. H. Bamford, D. L. Levi, and D. M. Newitt, *J. Chem. Soc.*, **1946**, 468–471.

<sup>5</sup> H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1–41 (1942).

<sup>6</sup> A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692–2696 (1947).

<sup>7</sup> Carbide and Carbon Chemicals Corporation, *Synthetic Organic Chemicals*, 11th Edition, New York, N. Y., 1942.

Table XVII is not intended to be entirely comprehensive; vapor pressures of some volatile compounds not included therein may be found by reference to the publications cited above.

There may be some uncertainty in the higher vapor pressure values owing to the difficulties of reading the diminishing log scale used in the graphical interpolations. Errors due to non-linearity of the data have been minimized as much as possible by interpolating within the narrowest temperature ranges available. The tabulated data are believed to be reasonably accurate, if the original experimental data are reliable. It is difficult to judge the accuracy of the latter, many of which have been measured with extreme care; but it is certain, as evidenced by extensive disagreement in the literature, that the measurement of vapor pressure is much easier than the purification of the compounds to be measured. In recognition of the probability that more accurate data may become available for many of the compounds listed, additional space has been provided for inserting such corrections as may be found desirable.

Table XVII includes data for 398 compounds. They are arranged alphabetically in order of the major elements. Thus all compounds of carbon with electronegative elements only are listed under carbon, but organometallic compounds are listed under their metallic components. All organic derivatives of boron and of silicon are listed under those elements. Table XVII begins on page 123.

TABLE VII. DATA FOR CS<sub>2</sub> VAPOR PRESSURE THERMOMETER

°C	mm	°C	mm	°C	mm	°C	mm
25	359.8	12	215.4	-1	121.6	-14	64.2
24	346.6	11	206.6	-2	116.0	-15	60.9
23	333.8	10	199.1	-3	110.7	-16	57.8
22	321.3	9	189.8	-4	105.6	-17	54.8
21	309.2	8	181.8	-5	100.7	-18	51.9
20	297.5	7	174.1	-6	95.9	-19	49.2
19	286.1	6	166.7	-7	91.4	-20	46.5
18	275.0	5	159.5	-8	87.0	-21	44.0
17	264.3	4	152.6	-9	82.8	-22	41.6
16	254.0	3	145.9	-10	78.8	-23	39.3
15	243.8	2	139.5	-11	74.9	-24	37.1
14	234.0	1	133.3	-12	71.2	-25	35.0
13	224.5	0	127.3	-13	67.6		



TABLE VIII. DATA FOR SO<sub>2</sub> VAPOR PRESSURE THERMOMETER

°C	mm	°C	mm	°C	mm	°C	mm
-10	759.8	-23	411.2	-36	205.1	-49	92.6
-11	726.6	-24	390.9	-37	193.6	-50	86.7
-12	694.6	-25	371.5	-38	182.6	-51	81.2
-13	663.7	-26	352.6	-39	172.2	-52	75.9
-14	633.9	-27	334.7	-40	162.5	-53	70.9
-15	605.3	-28	317.7	-41	152.9	-54	66.3
-16	577.7	-29	301.4	-42	143.9	-55	61.8
-17	551.0	-30	285.8	-43	135.4	-56	57.7
-18	525.3	-31	270.8	-44	127.3	-57	53.7
-19	500.6	-32	256.5	-45	119.6	-58	50.0
-20	476.7	-33	242.8	-46	112.3	-59	46.6
-21	453.9	-34	229.7	-47	105.4	-60	43.3
-22	432.1	-35	217.1	-48	98.8	-61	40.3

TABLE IX. DATA FOR NH<sub>3</sub> VAPOR PRESSURE THERMOMETER

°C	mm	°C	mm	°C	mm	°C	mm
-34	736.0	-45	409.7	-56	213.0	-67	102.0
-35	699.6	-46	387.2	-57	199.9	-68	95.0
-36	664.6	-47	365.7	-58	187.5	-69	88.4
-37	631.0	-48	345.2	-59	175.8	-70	82.2
-38	598.9	-49	325.7	-60	164.7	-71	76.3
-39	568.2	-50	307.1	-61	154.2	-72	70.8
-40	538.7	-51	289.4	-62	144.2	-73	65.6
-41	510.5	-52	272.5	-63	134.8	-74	60.7
-42	483.5	-53	256.5	-64	125.9	-75	56.2
-43	457.7	-54	241.3	-65	117.5	-76	52.0
-44	433.2	-55	226.8	-66	109.5	-77	48.0

TABLE X. DATA FOR CO<sub>2</sub> VAPOR PRESSURE THERMOMETER

°C	mm	°C	mm	°C	mm	°C	mm
-79	730.1	-87	367.1	-95	173.6	-103	76.2
-80	672.2	-88	335.6	-96	157.3	-104	68.3
-81	618.3	-89	306.3	-97	142.4	-105	61.2
-82	568.1	-90	279.2	-98	128.7	-106	54.7
-83	521.4	-91	254.3	-99	116.2	-107	48.9
-84	478.5	-92	231.5	-100	104.8	-108	43.6
-85	438.4	-93	210.5	-101	94.4	-109	38.9
-86	401.3	-94	191.2	-102	84.9	-110	34.6

TABLE XI. DATA FOR HCl VAPOR PRESSURE THERMOMETER

$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>
-85	760.9	-92	503.1	-99	320.1	-106	195.5
-86	718.7	-93	472.7	-100	299.1	-107	181.6
-87	678.4	-94	443.9	-101	279.3	-108	168.4
-88	640.0	-95	416.5	-102	260.6	-109	156.1
-89	603.3	-96	390.5	-103	242.8	-110	144.6
-90	568.2	-97	365.8	-104	226.0	-111	133.8
-91	534.9	-98	342.3	-105	210.2		

TABLE XII. DATA FOR  $\text{C}_2\text{H}_4$  VAPOR PRESSURE THERMOMETER

$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>
-104	747.0	-116	346.7	-128	138.9	-140	45.5
-105	704.7	-117	323.2	-129	127.6	-141	41.1
-106	664.1	-118	301.0	-130	117.0	-142	37.0
-107	625.2	-119	280.1	-131	107.2	-143	33.2
-108	588.0	-120	260.3	-132	98.0	-144	29.8
-109	552.4	-121	241.7	-133	89.5	-145	26.7
-110	518.4	-122	224.2	-134	81.6	-146	23.9
-111	485.9	-123	207.7	-135	74.3	-147	21.3
-112	455.0	-124	192.2	-136	67.6	-148	19.0
-113	425.7	-125	177.6	-137	61.4	-149	16.9
-114	397.9	-126	163.9	-138	55.6	-150	14.9
-115	371.6	-127	151.0	-139	50.3		

TABLE XIII. DATA FOR  $\text{CH}_4$  VAPOR PRESSURE THERMOMETER

$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>
-161	781.5	-167	467.2	-173	261.3	-179	134.0
-162	721.1	-168	426.2	-174	235.5	-180	118.5
-163	662.4	-169	387.9	-175	211.5	-181	104.7
-164	608.3	-170	352.3	-176	189.4	-182	92.3
-165	558.2	-171	319.6	-177	169.1	-183	81.1
-166	511.1	-172	289.2	-178	150.6	-184	71.0

TABLE XIV. DATA FOR  $\text{O}_2$  VAPOR PRESSURE THERMOMETER

$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>	$^{\circ}\text{C}$	<i>mm</i>
-183	757.2	-190	340.7	-197	129.9	-204	39.9
-184	681.4	-191	300.2	-198	111.3	-205	33.0
-185	611.6	-192	263.6	-199	95.0	-206	27.1
-186	547.4	-193	230.6	-200	80.7	-207	22.1
-187	488.5	-194	200.9	-201	68.2	-208	17.9
-188	434.6	-195	174.4	-202	57.3	-209	14.4
-189	385.5	-196	150.9	-203	48.0	-210	11.5

TABLE XV. DATA FOR N<sub>2</sub> VAPOR PRESSURE THERMOMETER

$^{\circ}\text{C}$	$\text{mm}$	$^{\circ}\text{C}$	$\text{mm}$	$^{\circ}\text{C}$	$\text{mm}$	$^{\circ}\text{C}$	$\text{mm}$
-196	741	-200	459	-204	254	-208	136
-197	657	-201	391	-205	218	-209	112.5
-198	580.5	-202	340	-206	183	-210	94
-199	511	-203	295	-207	158		

TABLE XVI. REFERENCE TABLE FOR COPPER-CONSTANTAN THERMOCOUPLES

<i>Temperature, <math>^{\circ}\text{C}</math></i>	<i>E, micro-volts</i>	<i>dE/dt</i>	<i>Temperature, <math>^{\circ}\text{C}</math></i>	<i>E, micro-volts</i>	<i>dE/dt</i>
0	0.0		-44	1600.4	
		38.4			34.1
-2	76.8		-46	1668.6	
		38.2			33.9
-4	153.2		-48	1736.3	
		38.0			33.7
-6	229.2		-50	1803.7	
		37.8			33.5
-8	304.8		-52	1870.6	
		37.6			33.3
-10	380.1		-54	1937.2	
		37.4			33.0
-12	455.0		-56	2003.3	
		37.3			32.8
-14	529.5		-58	2068.9	
		37.1			32.6
-16	603.7		-60	2134.2	
		36.9			32.4
-18	677.4		-62	2199.0	
		36.7			32.2
-20	750.8		-64	2263.4	
		36.5			32.0
-22	823.8		-66	2327.4	
		36.3			31.8
-24	896.3		-68	2391.0	
		36.1			31.6
-26	968.5		-70	2454.1	
		35.9			31.3
-28	1040.3		-72	2516.7	
		35.7			31.1
-30	1111.8		-74	2579.0	
		35.5			30.9
-32	1182.8		-76	2640.8	
		35.3			30.7
-34	1253.4		-78	2702.1	
		35.1			30.5
-36	1323.6		-80	2763.1	
		34.9			30.2
-38	1393.4		-82	2823.5	
		34.7			30.0
-40	1462.8		-84	2883.6	
		34.5			29.8
-42	1531.8		-86	2943.1	
		34.3			29.6

TABLE XVI. REFERENCE TABLE FOR COPPER-CONSTANTAN THERMOCOUPLES (*Continued*)

<i>Temperature, °C</i>	<i>E, microvolts</i>	<i>dE/dt</i>	<i>Temperature, °C</i>	<i>E, microvolts</i>	<i>dE/dt</i>
-88	3002.3		-142	4421.8	
		29.3			22.9
-90	3061.0		-144	4467.6	
		29.1			22.6
-92	3119.2		-146	4512.9	
		28.9			22.4
-94	3176.9		-148	4557.6	
		28.7			22.1
-96	3234.3		-150	4601.9	
		28.4			21.9
-98	3291.1		-152	4645.6	
		28.2			21.6
-100	3347.5		-154	4688.8	
		28.0			21.3
-102	3403.4		-156	4731.4	
		27.7			21.1
-104	3458.9		-158	4773.7	
		27.5			20.8
-106	3513.9		-160	4815.4	
		27.3			20.6
-108	3568.4		-162	4856.6	
		27.0			20.3
-110	3622.5		-164	4897.2	
		26.8			20.1
-112	3676.1		-166	4937.3	
		26.6			19.8
-114	3729.2		-168	4976.9	
		26.3			19.5
-116	3781.8		-170	5015.9	
		26.1			19.3
-118	3834.0		-172	5054.5	
		25.8			19.0
-120	3885.6		-174	5092.5	
		25.6			18.7
-122	3936.8		-176	5129.9	
		25.4			18.5
-124	3987.5		-178	5166.9	
		25.1			18.2
-126	4037.8		-180	5203.3	
		24.9			17.9
-128	4087.5		-182	5239.1	
		24.6			17.6
-130	4136.7		-184	5274.4	
		24.4			17.4
-132	4185.5		-186	5309.2	
		24.1			17.1
-134	4233.8		-188	5343.4	
		23.9			16.8
-136	4281.5		-190	5377.1	
		23.6			16.6
-138	4328.8		-192	5410.2	
		23.4			
-140	4375.6				
		23.1			

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
AlB <sub>3</sub> H <sub>12</sub> Aluminum borohydride	-64.5	45.9			19	120	286
Al(CH <sub>3</sub> ) <sub>3</sub> Aluminum trimethyl	15.0	125.3					8.8
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Aluminum triethyl		207.0					0.2
Sb(CH <sub>3</sub> ) <sub>3</sub> Antimony trimethyl	-62.0	80.6			5.0	34	85
Sb(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Antimony triethyl	-98.0	161.4				0.8	2.9
SbCl <sub>5</sub> Antimony pentachloride	2.8						0.9
AsH <sub>3</sub> Arsine	-116.3	-62.1	36	338			
CH <sub>3</sub> AsCl <sub>2</sub> Methyl arsenic dichloride	-59	134.5				2.2	7.8
AsCl <sub>3</sub> Arsenic trichloride	-18	130.4				2.3	8.1
Bc(BH <sub>4</sub> ) <sub>2</sub> Beryllium borohydride	123	90.0				0.9	5.2
Bi(CH <sub>3</sub> ) <sub>3</sub> Bismuth trimethyl	-85.8	107.1			1.2	10	29
BH <sub>3</sub> CO Borine carbonyl	-137.0	-64.0	25	322			
BH <sub>3</sub> N(CH <sub>3</sub> ) <sub>3</sub> Borine trimethylamine	94	171					0.7
B(CH <sub>3</sub> ) <sub>3</sub> Boron trimethyl		-20.1	1.5	29	423		
B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Boron triethyl		-56.2	123	433			

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (Continued)

FORMULA NAME	M P., °C	B P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
B(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> Boron tripropyl	-65.5	164.5				1.1	3.5
B(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> Boron triisopropyl	-52.5	147.4				1.6	5.3
BF <sub>3</sub> Boron trifluoride	-126.8	-110.7	292				
BCl <sub>3</sub> Boron trichloride	-107	12.7		3.9	96	470	
BBr <sub>3</sub> Boron tribromide	-45	91.7			2.0	18	54
B <sub>2</sub> H <sub>6</sub> Diborane	-169	-86.5	194				
CH <sub>3</sub> B <sub>2</sub> H <sub>5</sub> Methyl diborane				55			
(CH <sub>3</sub> ) <sub>2</sub> B <sub>2</sub> H <sub>4</sub> Dimethyl diborane	-150.2	-2.6	0.6	13	203		
(CH <sub>3</sub> ) <sub>3</sub> B <sub>2</sub> H <sub>3</sub> Trimethyl diborane	-122.9	45.5		0.7	21	125	
(CH <sub>3</sub> ) <sub>4</sub> B <sub>2</sub> H <sub>2</sub> Tetramethyl diborane	-72.5	68.6			6.9	48	123
B <sub>2</sub> H <sub>6</sub> Br Bromodiborane	-104.2	16.3		3.9	79	400	
B <sub>3</sub> N <sub>3</sub> H <sub>6</sub> Borazole	-58.2	50.6			11	85	213
B <sub>4</sub> H <sub>10</sub> Tetraborane	-119.9	16.1		3.2	76	390	
B <sub>5</sub> H <sub>9</sub> Pentaborane (stable)	-47.0	58.1			8.2	61	162
B <sub>5</sub> H <sub>11</sub> Pentaborane (unstable)		67.0			3.9	35	99

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
B <sub>6</sub> H <sub>10</sub> Hexaborane	-65					7.2	
Br <sub>2</sub> Bromine	-7.3	58.2			4.7	63	165
Cd(CH <sub>3</sub> ) <sub>2</sub> Cadmium dimethyl	-4.2	105.7				9.9	28
C <sub>2</sub> H <sub>6</sub> Ethane	-183.2	-88.6	212				
C <sub>3</sub> H <sub>8</sub> Propane	-187.1	-42.1	7.2	109			
C <sub>4</sub> H <sub>10</sub> Butane	-135	-0.5	0.4	9.1	181		
C <sub>4</sub> H <sub>10</sub> 2-Methylpropane	-145	-11.7	0.9	18	296		
C <sub>5</sub> H <sub>12</sub> Pentane	-129.7	36.1		0.8	31	185	427
C <sub>5</sub> H <sub>12</sub> 2-Methylbutane	-159.7	27.8		1.6	48	266	572
C <sub>5</sub> H <sub>12</sub> 2,2-Dimethylpropane	-16.6	9.5		8.8	134	534	
C <sub>6</sub> H <sub>14</sub> Hexane	-95.3	68.7			5.4	46	122
C <sub>6</sub> H <sub>14</sub> 2-Methylpentane	-154	60.3			9.2	66	167
C <sub>6</sub> H <sub>14</sub> 3-Methylpentane	-118	63.3			8.1	60	150
C <sub>6</sub> H <sub>14</sub> 2,2-Dimethylbutane	-99.8	49.7			17	111	265
C <sub>6</sub> H <sub>14</sub> 2,3-Dimethylbutane	-128.2	58.0			11	77	190

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>7</sub> H <sub>16</sub> Heptane	-90.6	98.4			1.1	11	36
C <sub>7</sub> H <sub>16</sub> 2-Methylhexane	-118.2	90.0			1.7	18	52
C <sub>7</sub> H <sub>16</sub> 2,2,3-Trimethylbutane	-25.0	80.9				31	82
C <sub>8</sub> H <sub>18</sub> Octane	-56.8	125.6				2.9	11
C <sub>8</sub> H <sub>18</sub> 2,2,3-Trimethylpentane	-112.3	109.8			0.7	8.0	25
C <sub>8</sub> H <sub>18</sub> 2,2,4-Trimethylpentane	-107.3	99.2			1.3	13	39
C <sub>8</sub> H <sub>18</sub> 2,2,3,3-Tetramethylbutane	-102.2					4.0	15
C <sub>9</sub> H <sub>20</sub> Nonane	-53.7	149.5				0.9	3.3
C <sub>10</sub> H <sub>22</sub> Decane	-29.7	173.0					1.2
C <sub>2</sub> H <sub>4</sub> Ethylene	-169	-103.7	462				
C <sub>3</sub> H <sub>6</sub> Propylene	-185	-47.7	12	146			
C <sub>4</sub> H <sub>8</sub> 1-Butene	-130	-6.3	0.5	13	231		
C <sub>4</sub> H <sub>8</sub> <i>cis</i> -2-Butene	-138.9	3.7	0.2	6.2	142	660	
C <sub>4</sub> H <sub>8</sub> <i>trans</i> -2-Butene	-105.4	0.9	0.4	8.1	167		
C <sub>4</sub> H <sub>8</sub> 2-Methylpropene	-140.3	-6.9	1.2	20	236		



TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>5</sub> H <sub>10</sub> 1-Pentene		30.1		1.2	42	233	532
C <sub>5</sub> H <sub>10</sub> 2-Methyl-1-butene	-135	20.2		3.2	75	362	
C <sub>5</sub> H <sub>10</sub> 2-Methyl-2-butene	-133	38.5		0.7	27	161	379
C <sub>6</sub> H <sub>12</sub> 1-Hexene	-98.5	66.0			7.0	53	140
C <sub>7</sub> H <sub>14</sub> 2-Heptene		98.5			1.2	12	37
C <sub>2</sub> H <sub>2</sub> Acetylene	-81.5	-84.0	67				
C <sub>4</sub> H <sub>6</sub> 1,2-Butadiene		18.5		3.3	77	373	
C <sub>4</sub> H <sub>6</sub> 1,3-Butadiene	-108.9	4.5	0.5	11	206		
C <sub>5</sub> H <sub>8</sub> 1,3-Pentadiene		42.1		0.5	22	142	330
C <sub>5</sub> H <sub>8</sub> 1,4-Pentadiene		26.1		1.6	49	276	604
C <sub>5</sub> H <sub>8</sub> 2-Methyl-1,3-butadiene	-146.7	32.6		1.2	38	212	485
C <sub>6</sub> H <sub>6</sub> Benzene	5.5	80.1			1.4	25	76
C <sub>7</sub> H <sub>8</sub> Toluene	-95.0	110.6				6.9	22
C <sub>8</sub> H <sub>10</sub> <i>o</i> -Xylene	-25.2	144.4				1.3	5.0
C <sub>8</sub> H <sub>10</sub> <i>m</i> -Xylene	-47.9	139.1				1.6	6.1

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (Continued)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>8</sub> H <sub>10</sub> <i>p</i> -Xylene	13.3	138.3				1.8	6.6
C <sub>8</sub> H <sub>10</sub> Ethylbenzene	-94.9	136.2				2.0	7.0
C <sub>8</sub> H <sub>8</sub> Styrene	-30.6	145.2				1.6	5.6
C <sub>9</sub> H <sub>12</sub> Isopropylbenzene	-96.0	152.4				0.8	3.2
C <sub>10</sub> H <sub>14</sub> <i>t</i> -Butylbenzene	-58	168.5					1.6
C <sub>3</sub> H <sub>6</sub> Cyclopropane	-126.6	-33.5	2.4	55			
C <sub>4</sub> H <sub>8</sub> Cyclobutane	-50	12.9		4.0	95	465	
C <sub>4</sub> H <sub>6</sub> Cyclobutene		2.4	0.3	7.6	153	693	
C <sub>5</sub> H <sub>10</sub> Cyclopentane	-93.7	49.3			16	107	259
C <sub>6</sub> H <sub>12</sub> Methylcyclopentane	-142.4	71.8			5.2	42	110
C <sub>7</sub> H <sub>14</sub> Ethylcyclopentane	-138.6	103.4			0.9	10	31
C <sub>6</sub> H <sub>12</sub> Cyclohexane	6.6	80.7			2.7	27	77
C <sub>7</sub> H <sub>14</sub> Methylcyclohexane	-126.4	100.9			1.2	12	36
C <sub>8</sub> H <sub>16</sub> Ethylcyclohexane	-111.3	131.8				2.7	9.8
C <sub>10</sub> H <sub>18</sub> <i>trans</i> -Decalin	-30.7	186.7				1.0	3.0

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
CH <sub>3</sub> Cl Methyl chloride	-97.7	-24.0		33	506		
CH <sub>2</sub> Cl <sub>2</sub> Dichloromethane	-96.7	40.7		0.5	20	137	338
CHCl <sub>3</sub> Chloroform	-63.5	61.3			7.5	58	153
CCl <sub>4</sub> Carbon tetrachloride	-22.6	76.7			3.9	32	87
CH <sub>3</sub> Br Methyl bromide	-93	3.6		6.0	140	662	
CH <sub>2</sub> Br <sub>2</sub> Dibromomethane	-52.8	98.6			1.2	12	34
CHBr <sub>3</sub> Bromoform	8.5	150.5					4.4
CH <sub>3</sub> I Methyl iodide	-64.4	42.4		0.7	23	139	325
C <sub>2</sub> H <sub>3</sub> Cl 1-Chloroethylene	-153.7	-13.8	0.6	16	302		
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> 1,1-Dichloroethylene	-122.5	31.7		1.0	35	211	497
C <sub>2</sub> HCl <sub>3</sub> Trichloroethylene	-73	86.7			2.4	21	60
C <sub>2</sub> Cl <sub>4</sub> Tetrachloroethylene	-19.0	120.8				4.3	14
C <sub>2</sub> H <sub>3</sub> Br Bromoethylene	-138	15.8		4.7	94	421	
C <sub>2</sub> H <sub>5</sub> Cl Ethyl chloride	-139	12.3		3.4	93	475	
C <sub>2</sub> H <sub>5</sub> Br Ethyl bromide	-117.8	38.4		0.7	25	165	384

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>2</sub> H <sub>5</sub> I Ethyl iodide	-105	72.4			5.2	42	110
C <sub>3</sub> H <sub>7</sub> Cl 1-Chloropropane	-122.8	46.4		0.5	16	114	273
C <sub>3</sub> H <sub>7</sub> Cl 2-Chloropropane	-117	36.5		1.2	35	189	433
C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub> 1,2-Dichloropropane		96.3					40
C <sub>3</sub> H <sub>7</sub> Br 1-Bromopropane	-109.9	71.0			5.0	39	110
C <sub>3</sub> H <sub>7</sub> Br 2-Bromopropane	-89.0	60.0			9.2	68	170
C <sub>3</sub> H <sub>7</sub> I 1-Iodopropane	-98.8	102.5			1.3	11	33
C <sub>3</sub> H <sub>7</sub> I 2-Iodopropane	-90	89.5			2.3	20	56
C <sub>4</sub> H <sub>9</sub> Cl 1-Chlorobutane	-123.1	77.8			3.7	31	83
C <sub>4</sub> H <sub>9</sub> Cl Isobutyl chloride	-131.2	68.9			5.3	44	120
C <sub>4</sub> H <sub>9</sub> Cl <i>sec</i> -Butyl chloride	-131.3	68.0			7.6	51	130
C <sub>4</sub> H <sub>9</sub> Cl <i>tert</i> -Butyl chloride	-26.5	51.0				105	251
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> 1,2-Dichlorobutane		123.5				5.1	16
C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> 2,3-Dichlorobutane	-80.4	116.0			0.5	5.8	19
C <sub>4</sub> H <sub>9</sub> Br 1-Bromobutane	-112.4	101.6			1.0	10	31

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>6</sub> H <sub>5</sub> F Fluorobenzene	-42.1	84.7				21	60
C <sub>6</sub> H <sub>5</sub> Cl Chlorobenzene	-45.2	132.2				2.6	8.8
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> <i>o</i> -Dichlorobenzene	-17.6	179.0					1.0
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> <i>m</i> -Dichlorobenzene	-24.2	173.0					1.6
C <sub>6</sub> H <sub>5</sub> Br Bromobenzene	-30.7	156.2				0.8	3.1
C <sub>7</sub> H <sub>7</sub> Cl <i>o</i> -Chlorotoluene		159.3					2.6
C <sub>7</sub> H <sub>7</sub> Cl <i>m</i> -Chlorotoluene		162.3					2.7
C <sub>7</sub> H <sub>7</sub> Cl <i>p</i> -Chlorotoluene	7.3	162.3					2.6
C <sub>7</sub> H <sub>7</sub> Br <i>m</i> -Bromotoluene	-39.8	183.7					1.3
C <sub>7</sub> H <sub>7</sub> Br <i>p</i> -Bromotoluene	28.5	184.5					1.6
CH <sub>3</sub> OH Methyl alcohol	-97.8	64.7			2.7	30	94
C <sub>2</sub> H <sub>5</sub> OH Ethyl alcohol	-112	78.4			0.9	12	42
ClCH <sub>2</sub> CH <sub>2</sub> OH Ethylene chlorohydrin	-69	128.8				1.3	5.2
C <sub>3</sub> H <sub>7</sub> OH Propyl alcohol	-127	97.8				3.4	14
C <sub>3</sub> H <sub>7</sub> OH Isopropyl alcohol	-85.8	82.5			0.6	8.4	31

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (Continued)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
CH <sub>3</sub> CHOHCH <sub>2</sub> Cl Propylene chlorohydrin		127.4					4.9
C <sub>4</sub> H <sub>9</sub> OH Butyl alcohol	-79.9	117.5				1.1	5.0
C <sub>4</sub> H <sub>9</sub> OH Isobutyl alcohol	-108	108.0				2.1	9.0
C <sub>4</sub> H <sub>9</sub> OH <i>sec</i> -Butyl alcohol	-114.7	99.5				2.9	12
C <sub>4</sub> H <sub>9</sub> OH <i>tert</i> -Butyl alcohol	25.3	82.9				6.5	29
C <sub>5</sub> H <sub>12</sub> OH Amyl alcohol		137.8					1.7
C <sub>5</sub> H <sub>11</sub> OH Isoamyl alcohol	-117.2	130.6					2.2
C <sub>5</sub> H <sub>11</sub> OH 2-Pentanol		119.7				0.9	4.3
C <sub>5</sub> H <sub>11</sub> OH <i>tert</i> -Amyl alcohol	-11.9	101.7				2.9	12
C <sub>3</sub> H <sub>5</sub> OH Allyl alcohol	-129	96.6				4.8	18
C <sub>6</sub> H <sub>13</sub> OH 1-Hexanol	-51.6	157.0					0.8
C <sub>6</sub> H <sub>13</sub> OH 2-Hexanol		139.9					1.6
C <sub>6</sub> H <sub>13</sub> OH 3-Hexanol		135.5				0.8	3.4
C <sub>6</sub> H <sub>13</sub> OH 2-Methyl-1-pentanol		147.9					1.4
C <sub>6</sub> H <sub>13</sub> OH 2-Methyl-2-pentanol	-103	121.1				1.4	6.2

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>6</sub> H <sub>13</sub> OH 2-Methyl-4-pentanol		131.7				1.0	4.3
C <sub>6</sub> H <sub>13</sub> OH 2-Ethyl-1-butanol		148.9					1.1
(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> COCH <sub>3</sub> Diacetone alcohol		167.9					1.2
ClC <sub>6</sub> H <sub>4</sub> OH o-Chlorophenol	7	174.5					1.7
HCHO Formaldehyde	-92	-19.5	1.0	22	392		
CH <sub>3</sub> CHO Acetaldehyde	-123.5	20.2		1.5	53	321	
CH <sub>3</sub> CHNOH Acetaldoxime		115.0				1.7	6.9
Cl <sub>3</sub> CCHO Chloral	-57	97.7			1.5	13	39
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO Butyraldehyde		75.7					91.5
C <sub>3</sub> H <sub>5</sub> CHO Crotonaldehyde		102.3					30
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CHCHO 2-Ethylbutyraldehyde		116.8					14
C <sub>4</sub> H <sub>3</sub> OCHO Furfural	-36.5	161.8					1.2
C <sub>6</sub> H <sub>12</sub> O <sub>3</sub> Paraformaldehyde	155	124.0				2.0	7.8
C <sub>6</sub> H <sub>13</sub> CHO Enanthaldehyde	-42	155.0					1.9
CH <sub>3</sub> COCH <sub>3</sub> Acetone	-94.6	56.5			8.4	67	177

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub> 2-Butanone	-85.9	79.6			3.4	30	79
CH <sub>3</sub> COC <sub>3</sub> H <sub>7</sub> 2-Pentanone	-77.8	103.3				2.6	13
C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub> 3-Pentanone	-42	102.7				2.9	12
C <sub>6</sub> H <sub>10</sub> O 3-Methyl-2-butanone	-92	88.9				5.5	22
CH <sub>3</sub> COC <sub>4</sub> H <sub>9</sub> 2-Hexanone	-56.9	127.5				0.6	2.6
C <sub>6</sub> H <sub>12</sub> O 4-Methyl-2-pentanone	-84.7	119.0				1.1	4.1
C <sub>6</sub> H <sub>10</sub> O Mesityl oxide	-59	130.0				1.9	7.0
C <sub>6</sub> H <sub>10</sub> O Cyclohexanone	-45.0	155.6				0.9	3.4
C <sub>7</sub> H <sub>14</sub> O 2,5-Dimethyl-3-pentanone		123.7				0.7	3.1
C <sub>9</sub> H <sub>18</sub> O Diisobutyl ketone		168.1					1.7
CH <sub>3</sub> OCH <sub>3</sub> Dimethyl ether	-138.5	-23.7	1.5	34	496		
C <sub>2</sub> H <sub>4</sub> O Ethylene oxide	-111.3	10.7		3.3	94	500	
CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> Methyl ethyl ether		7.5		3.9	108	565	
CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> OH 2-Methoxyethanol		124.4				2.6	8.9
C <sub>3</sub> H <sub>6</sub> O Propylene oxide	-112.1	34.5		0.8	28	183	437



TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> Dioxolane		74					70
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> 1,4-Dioxane	10	101.3			1.2	10	30
C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub> Diethyl ether	-116.3	34.6		0.7	27	183	436
C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>4</sub> OH 2-Ethoxyethanol		135.1					3.8
ClC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>4</sub> Cl 2,2'-Dichlorodiethyl ether		178.5					0.7
CH <sub>3</sub> OC <sub>3</sub> H <sub>7</sub> Methyl propyl ether		39.1		0.6	22	153	363
C <sub>4</sub> H <sub>8</sub> O Divinyl ether						234	553
C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> 1,2-Dimethoxyethane		93.0			3.1	24	61
C <sub>4</sub> H <sub>8</sub> O 1,2-Epoxy-2-methyl- propane		55.5		0.5	15	95	220
C <sub>2</sub> H <sub>5</sub> OC <sub>3</sub> H <sub>7</sub> Ethyl propyl ether		61.7			11	73	175
C <sub>3</sub> H <sub>7</sub> OC <sub>3</sub> H <sub>7</sub> Dipropyl ether	-122	89.5			2.1	20	56
C <sub>6</sub> H <sub>14</sub> O Diisopropyl ether	-60	67.5			6.6	50	135
C <sub>6</sub> H <sub>12</sub> O Allyl propyl ether		90.5			1.6	16	48
C <sub>6</sub> H <sub>12</sub> O Allyl isopropyl ether		79.5			2.3	22	64
C <sub>4</sub> H <sub>9</sub> OC <sub>2</sub> H <sub>4</sub> OH 2-Butoxyethanol		171.2					0.6

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>6</sub> H <sub>14</sub> O <sub>2</sub> Acetal		102.2			0.4	5.8	21
C <sub>6</sub> H <sub>14</sub> O <sub>2</sub> 1,2-Diethoxyethane		119.5			1.0	9.2	26
C <sub>6</sub> H <sub>14</sub> O <sub>3</sub> Di(2-methoxyethyl)ether		159.8					1.6
C <sub>7</sub> H <sub>8</sub> O Anisole	-37.3	155.5					2.7
C <sub>8</sub> H <sub>18</sub> O Dibutyl ether		142.2					4.8
C <sub>8</sub> H <sub>18</sub> O <sub>2</sub> 1,2-Dipropoxyethane		180.0			1.4	8.1	19
HCOOH Formic acid	8.2	100.6				8.4	33
CH <sub>3</sub> COOH Acetic acid	16.7	118.1				3.3	12
(CH <sub>3</sub> CO) <sub>2</sub> O Acetic anhydride	-73	139.6				0.9	3.6
C <sub>2</sub> Cl <sub>3</sub> OBr Trichloroacetyl bromide		143.0				1.7	5.8
C <sub>2</sub> H <sub>5</sub> COOH Propionic acid	-22	141.1				0.7	3.0
C <sub>3</sub> H <sub>7</sub> COOH Butyric acid		163.7					0.8
HCOOCH <sub>3</sub> Methyl formate	-99.8	32.0		0.7	30	193	472
HCOOC <sub>2</sub> H <sub>5</sub> Ethyl formate	-79	54.3			9.4	76	200
CH <sub>3</sub> COOCH <sub>3</sub> Methyl acetate	-98.7	57.8			7.4	58	164

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (Continued)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> Ethyl acetate	-82.4	77.1			2.4	24	72
CH <sub>3</sub> COOC <sub>2</sub> H <sub>3</sub> Vinyl acetate		72.5			3.4	30	85
C <sub>2</sub> H <sub>5</sub> COOCH <sub>3</sub> Methyl propionate	-87.5	79.8			2.1	21	64
C <sub>2</sub> H <sub>3</sub> COOCH <sub>3</sub> Methyl acrylate		80.2			2.4	23	69
HCOOC <sub>3</sub> H <sub>7</sub> Propyl formate	-92.9	81.3			2.3	22	64
HCOOC <sub>3</sub> H <sub>7</sub> Isopropyl formate		68.3			4.8	41	110
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CO <sub>3</sub> Diethyl carbonate	-43	125.8				2.1	7.9
HCOOC <sub>4</sub> H <sub>9</sub> Butyl formate		106.0			0.5	6.8	22
HCOOC <sub>4</sub> H <sub>9</sub> <i>sec</i> -Butyl formate		93.6			1.1	12	37
HCOOC <sub>4</sub> H <sub>9</sub> Isobutyl formate	-95.3	98.2			0.9	11	32
HCOOC <sub>4</sub> H <sub>9</sub> <i>tert</i> -Butyl formate		98.0			0.9	11	34
C <sub>3</sub> H <sub>7</sub> COOCH <sub>3</sub> Methyl butyrate		102.3			0.6	7.5	23
C <sub>3</sub> H <sub>7</sub> COOCH <sub>3</sub> Methyl isobutyrate	-84.7	92.6			1.1	12	38
CH <sub>3</sub> COOC <sub>3</sub> H <sub>7</sub> Propyl acetate	-92.5	101.8			0.5	7.3	25
CH <sub>3</sub> COOC <sub>3</sub> H <sub>7</sub> Isopropyl acetate		89.0			1.5	16	47

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>2</sub> H <sub>5</sub> COOC <sub>2</sub> H <sub>5</sub> Ethyl propionate	-72.6	99.1			0.6	8.1	28
C <sub>2</sub> H <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> Ethyl acrylate	-71.2	99.5			0.7	9.0	29
C <sub>5</sub> H <sub>8</sub> O <sub>2</sub> Methyl methacrylate		101.0			0.8	9.5	30
C <sub>2</sub> H <sub>3</sub> COOC <sub>4</sub> H <sub>9</sub> Butyl acrylate	-64.6	147.4				1.0	4.0
C <sub>7</sub> H <sub>16</sub> O <sub>3</sub> Triethylorthoformate		146.0				0.7	2.7
CH <sub>3</sub> HS Methyl mercaptan	-121	6.8		3.8	109	577	
C <sub>2</sub> H <sub>5</sub> HS Ethyl mercaptan	-121	35.0		1.0	32	188	438
C <sub>3</sub> H <sub>7</sub> HS Propyl mercaptan	-112	67.4			6.1	48	123
C <sub>6</sub> H <sub>6</sub> S Thiophenol		168.0					1.2
(CH <sub>3</sub> ) <sub>2</sub> S Dimethyl sulfide	-83.2	36.0		1.0	30	178	423
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S Diethyl sulfide	-99.5	88.0			1.7	16	49
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Se Diethyl selenide		108.0			0.5	6.6	22
C <sub>6</sub> H <sub>10</sub> S Diallyl sulfide	-83	138.6				1.9	6.8
C <sub>4</sub> H <sub>4</sub> S Thiophene	-38.3	84.4			2.0	20	60
C <sub>4</sub> H <sub>4</sub> Se Selenophene		114.3			1.7	12	33

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>6</sub> H <sub>6</sub> S 2-Methylthiophene	-63.5	112.5				7.1	22
C <sub>6</sub> H <sub>6</sub> S 3-Methylthiophene	-68.9	115.4				5.8	18
CH <sub>3</sub> SCN Methyl thiocyanate	-51	132.9				2.8	9.7
CH <sub>3</sub> NCS Methyl isothiocyanate	35.5	119.0			1.1	7.6	20
C <sub>2</sub> H <sub>5</sub> NCS Ethyl isothiocyanate	-5.9	131.0				2.6	8.6
C <sub>3</sub> H <sub>5</sub> NCS Allyl isothiocyanate	-80	150.7				1.1	3.7
CH <sub>3</sub> NH <sub>2</sub> Methyl amine	-93.5	-6.3		6.5	190		
(CH <sub>3</sub> ) <sub>2</sub> NH Dimethyl amine	-96	7.4		2.8	96	565	
(CH <sub>3</sub> ) <sub>3</sub> N Trimethylamine	-117.1	2.9		6.6	145	682	
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> Ethylamine	-80.6	16.6		1.7	60	370	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH Diethylamine	-38.9	55.5			9.8	74	192
NH <sub>2</sub> C <sub>2</sub> H <sub>4</sub> NH <sub>2</sub> Ethylenediamine		117.2					11
C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> Propylamine	-83	48.5		0.3	13	98	250
CH <sub>3</sub> CH(NH <sub>2</sub> )CH <sub>2</sub> NH <sub>2</sub> Propylenediamine		119.7					9.4
C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> Isobutylamine	-85.0	68.6			4.2	37	106

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
O:(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> :NH Morpholine		128.9					8.0
(CH <sub>3</sub> ) <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OH Dimethylethanolamine		133.5					10
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NC <sub>2</sub> H <sub>4</sub> OH Diethylethanolamine		162.1					1.4
C <sub>8</sub> H <sub>19</sub> N Diisobutylamine	-70	139.5				1.5	5.5
C <sub>5</sub> H <sub>5</sub> N Pyridine	-42	115.4				4.3	15
ClC <sub>5</sub> H <sub>4</sub> N 2-Chloropyridine		170.2					1.6
BrC <sub>5</sub> H <sub>4</sub> N 3-Bromopyridine		173.4					1.2
C <sub>6</sub> H <sub>11</sub> N Piperidine	-9	106.0				7.9	25
C <sub>6</sub> H <sub>7</sub> N 2-Picoline	-70	128.8					4.8
CH <sub>3</sub> CN Acetonitrile	-41	81.8			3.2	27	73
C <sub>2</sub> H <sub>5</sub> CN Propionitrile	-91.9	97.1			1.2	12	36
C <sub>2</sub> H <sub>3</sub> CN Acrylonitrile	-82	78.5			4.2	33	88
C <sub>4</sub> H <sub>5</sub> N Methacrylonitrile		90.3			2.5	20	56
C <sub>4</sub> H <sub>5</sub> N 3-Butenenitrile		119.0				4.0	14
C <sub>4</sub> H <sub>7</sub> N Butyronitrile		117.5			0.3	4.3	15

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	<i>M P.</i> , °C	<i>B.P.</i> , °C	<i>Pressure, mm Hg</i>				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
C <sub>7</sub> H <sub>5</sub> N Phenyl isocyanide		165.0					1.8
C <sub>7</sub> H <sub>5</sub> NO Phenyl isocyanate		165.6					1.9
CH <sub>3</sub> NO <sub>2</sub> Nitromethane	-29	101.2				8.4	27
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub> Nitroethane	-90	114.0				4.5	15
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub> 1-Nitropropane	-108	131.6				2.0	7.4
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub> 2-Nitropropane	-93	120.3				3.8	13
C <sub>8</sub> H <sub>11</sub> NO <sub>3</sub> Isoamylnitrate		147.5					2.8
CO <sub>2</sub> Carbon dioxide	-57.5	-78.5	26	760			
COCl <sub>2</sub> Phosgene	-104	8.3		4.4	113	560	
COS Carbon oxysulfide	-138.8	-49.9	12	164			
COSe Carbon oxyselenide		-21.9	2.0	34	442		
CS <sub>2</sub> Carbon disulfide	-111.8	46.5		0.6	21	127	295
CSSe Carbon sulfoselenide	-75.2	85.6			3.1	26	69
C <sub>2</sub> N <sub>2</sub> Cyanogen	-34.4	-21.0		8.4	380		
CNCl Cyanogen chloride	-6.5	13.1		0.9	53	443	

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
CNBr Cyanogen bromide	58	61.5			1.3	22	86
C <sub>3</sub> O <sub>2</sub> Carbon suboxide	-107	6.3		5.2	122	590	
C <sub>3</sub> S <sub>2</sub> Carbon subsulfide	0.4						1.5
Cl <sub>2</sub> Chlorine	-100.7	-33.8	2.5	62			
Cl <sub>2</sub> O Chlorine monoxide	-116	2.2		6.5	138	706	
ClO <sub>2</sub> Chlorine dioxide	-59	11.1			79	492	
Co(CO) <sub>3</sub> NO Cobalt nitrosyl tricarbonyl	-11	80.0				22	64
CrO <sub>2</sub> Cl <sub>2</sub> Chromyl chloride		117.1				4.0	14
Ga(CH <sub>3</sub> ) <sub>3</sub> Gallium trimethyl	-19	55.6			8.8	66	176
GeH <sub>4</sub> Germanium hydride, germane	-165	-88.9	194				
Ge(CH <sub>3</sub> ) <sub>4</sub> Germanium tetramethyl	-88	44.0		0.7	21	136	318
GeHCl <sub>3</sub> Trichlorogermane	-71.1	75.0			2.1	24	72
GeCl <sub>4</sub> Germanium tetrachloride	-49.5	84.0			2.7	25	70
Ge <sub>2</sub> H <sub>6</sub> Digermane	-109	31.5		2.5	53	243	507
Ge <sub>3</sub> H <sub>8</sub> Trigermane	-105.6	110.8			1.3	11	30



TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
HCl Hydrogen chloride	-114.3	-84.8	120				
HBr Hydrogen bromide	-87.0	-66.5	27	387			
HI Hydrogen iodide	-50.9	-35.1	4.0	67			
HCN Hydrogen cyanide	-13.2	25.9			32	260	603
H <sub>2</sub> O Water	0.0	100.0				4.6	17
H <sub>2</sub> O <sub>2</sub> Hydrogen peroxide	-0.9						1.4
H <sub>2</sub> S Hydrogen sulfide	-85.5	-60.4	16	259			
H <sub>2</sub> S <sub>2</sub> Hydrogen disulfide	-89.7	64.0			2.4	28	90
H <sub>2</sub> Se Hydrogen selenide	-64	-41.1	1.8	69			
H <sub>2</sub> Te Hydrogen telluride	-49.0	-2.0		7.4	190		
Fe(CO) <sub>5</sub> Iron pentacarbonyl	-21	105.0				6.4	13
Pb(CH <sub>3</sub> ) <sub>4</sub> Lead tetramethyl	-27.5	110.0			0.8	7.7	24
Ni(CO) <sub>4</sub> Nickel carbonyl	-25	42.5				134	318
NH <sub>3</sub> Ammonia	-77.7	-33.4	0.6	44			
NOCl Nitrosyl chloride	-64.5	-6.4			207		

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
N <sub>2</sub> O Nitrous oxide	-90.9	-88.5	84				
N <sub>2</sub> O <sub>4</sub> Nitrogen tetroxide	-9.3	21.0			9.0	53	713
N <sub>2</sub> O <sub>5</sub> Nitrogen pentoxide	30	32.4			1.5	51	281
PH <sub>3</sub> Phosphine	-132.5	-87.5	171				
PCl <sub>3</sub> Phosphorus trichloride	-111.8	74.2			4.2	35	96
PBr <sub>3</sub> Phosphorus tribromide	-40	175.3					2.1
POCl <sub>3</sub> Phosphorus oxychloride	2	105.1					27
PSCl <sub>3</sub> Phosphorus thiochloride	-36.2	124.0				3.8	12
Rn Radon	-71	-61.8	38	340			
SiH <sub>4</sub> Silane	-185	-111.5					
SiH <sub>3</sub> CH <sub>3</sub> Methylsilane		-56.9	21	255			
SiH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> Ethylsilane		-14	1.3	23	324		
SiH <sub>3</sub> C <sub>3</sub> H <sub>7</sub> Propylsilane		23		2.8	60	308	680
SiH <sub>3</sub> C <sub>4</sub> H <sub>9</sub> Butylsilane		55			12	78	196
SiH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> Phenylsilane		120			0.9	7.2	20

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
SiH <sub>3</sub> Cl Chlorosilane		-30.4	2.3	50	668		
SiH <sub>3</sub> Br Bromosilane	-93.9	2.4		9.0	157	698	
SiH <sub>3</sub> I Iodosilane	-57.0	45.4		0.6	20	124	292
SiH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> Dimethylsilane		-20.1	1.8	33	434		
SiH <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Diethylsilane		54			12	80	202
SiH <sub>2</sub> (C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Dipropylsilane		111			0.9	8.0	23
SiH <sub>2</sub> CH <sub>3</sub> Cl Chloromethylsilane		8.7		5.2	117	548	
SiH <sub>2</sub> Br <sub>2</sub> Dibromosilane	-70.2	70.5			7.7	52	125
SiHCH <sub>3</sub> Cl <sub>2</sub> Dichloromethylsilane		41.9		0.8	26	154	347
SiHCl <sub>3</sub> Trichlorosilane	-126.6	31.8		1.3	39	218	500
SiHBr <sub>3</sub> Tribromosilane	-73.5	111.8			0.8	8.1	24
Si(CH <sub>3</sub> ) <sub>4</sub> Silicon tetramethyl	-102.1	27.0		1.9	50	271	590
SiC <sub>2</sub> H <sub>14</sub> Ethyltrimethylsilane		62.0			9.1	64	161
SiC <sub>3</sub> H <sub>16</sub> Propyltrimethylsilane		90.0			2.7	22	61
SiC <sub>4</sub> H <sub>18</sub> Butyltrimethylsilane		115.0				5.5	18

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (Continued)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
SiC <sub>7</sub> H <sub>18</sub> Triethylmethylsilane		127.0				3.6	12
SiC <sub>8</sub> H <sub>20</sub> Amyltrimethylsilane		139.0				1.9	6.9
SiC <sub>8</sub> H <sub>12</sub> Dimethylphenylsilane		159.3				0.7	2.7
SiC <sub>8</sub> H <sub>20</sub> Tetraethylsilane		153.0				1.1	3.9
SiC <sub>6</sub> H <sub>14</sub> O Ethoxytrimethylsilane		75.7			4.3	33	91
SiC <sub>6</sub> H <sub>16</sub> O <sub>2</sub> Diethoxydimethylsilane		113.5				4.6	15
SiC <sub>7</sub> H <sub>18</sub> O <sub>3</sub> Triethoxymethylsilane		143.5				1.1	4.2
Si(CH <sub>3</sub> ) <sub>3</sub> Cl Trimethylchlorosilane		57.9			10	74	186
Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Cl Triethylchlorosilane		146.3				1.4	5.1
Si(CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> Dimethyldichlorosilane	—86.0	70.3			5.2	41	113
Si(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> Diethyldichlorosilane		130.4				1.9	7.1
SiC <sub>6</sub> H <sub>10</sub> Cl <sub>2</sub> Allyldichloroethylsilane		150.3				1.2	4.5
SiC <sub>6</sub> H <sub>10</sub> Cl <sub>2</sub> Diallyldichlorosilane		165.3					2.0
SiCH <sub>3</sub> (OC <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> Methylethoxydichlorosilane		100.6			1.1	11	32
SiCH <sub>3</sub> Cl <sub>3</sub> Methyltrichlorosilane	—90	66.4			8.2	57	142

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
SiC <sub>2</sub> H <sub>5</sub> Cl <sub>3</sub> Ethyltrichlorosilane	-40	99.5			0.6	7.5	26
SiC <sub>3</sub> H <sub>7</sub> Cl <sub>3</sub> Isopropyltrichlorosilane		118.5				5.4	18
SiC <sub>3</sub> H <sub>5</sub> Cl <sub>3</sub> Allyltrichlorosilane		118.0				4.3	14
Si(OC <sub>2</sub> H <sub>5</sub> )Cl <sub>3</sub> Ethoxytrichlorosilane		102.4			1.0	10	31
SiF <sub>4</sub> Silicon tetrafluoride	-90	-94.8	118				
SiCl <sub>4</sub> Silicon tetrachloride	-68.8	56.8			11	76	191
Si <sub>2</sub> H <sub>6</sub> Disilane	-132.6	-14.3	1.6	28	332		
Si <sub>2</sub> Cl <sub>6</sub> Hexachlorodisilane	-1.2	139.0					3.1
Si <sub>2</sub> H <sub>6</sub> O Disiloxane	-144.2	-15.4	1.0	21	331		
Si <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> O 1,3-Dichlorotetramethyl- disiloxane	-37	138.0				1.7	6.1
Si <sub>2</sub> Cl <sub>6</sub> O Hexachlorodisiloxane	-33.2	135.6				1.4	5.6
Si <sub>2</sub> CH <sub>9</sub> N 2-Methyldisilazane		34.0		1.0	32	190	450
Si <sub>2</sub> C <sub>2</sub> H <sub>11</sub> N 2-Ethyldisilazane	-127	65.9			9.1	61	150
Si <sub>3</sub> H <sub>8</sub> Trisilane	-117.2	53.1			15	93	218
Si <sub>3</sub> H <sub>9</sub> N Trisilazane	-105.7	48.7			15	107	256

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	M.P., °C	B.P., °C	Pressure, mm Hg				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
Si <sub>4</sub> H <sub>10</sub> Tetrasilane	-93.6	100.0			0.6	7.6	25
SO <sub>2</sub> Sulfur dioxide	-73.2	-10.0		8.4	225		
SO <sub>3</sub> Sulfur trioxide (alpha)	16.8	44.8			1.8	44	195
Sulfur trioxide (beta)	32.3	44.8			1.1	30	150
Sulfur trioxide (gamma)	62.1	51.6				6.3	53
S <sub>2</sub> Cl <sub>2</sub> Sulfur monochloride	-80	138.0				1.7	6.4
SOCl <sub>2</sub> Thionyl chloride	-104.5	75.4			4.7	36	94
SOBr <sub>2</sub> Thionyl bromide	-52.2	139.5				1.6	5.4
SO <sub>2</sub> Cl <sub>2</sub> Sulfuryl chloride	-54.1	69.2			5.6	42	110
Tl(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Thallium triethyl	-63.0	192.1					1.9
SnH <sub>4</sub> Stannane	-149.9	-52.3	18	193			
SnH <sub>3</sub> CH <sub>3</sub> Methylstannane		0	0.5	11	173	760	
SnH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> Dimethylstannane		35		1.2	32	184	
SnH(CH <sub>3</sub> ) <sub>3</sub> Trimethylstannane		59			11	71	175
Sn(CH <sub>3</sub> ) <sub>4</sub> Tin tetramethyl		-78.0			4.3	34	88
SnC <sub>6</sub> H <sub>14</sub> Ethyltrimethyltin		108.8			0.8	8.0	25

TABLE XVII. VAPOR PRESSURES OF PURE COMPOUNDS (*Continued*)

FORMULA NAME	<i>M.P.</i> , °C	<i>B.P.</i> , °C	<i>Pressure, mm Hg</i>				
			CS <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	20°
SnC <sub>6</sub> H <sub>11</sub> Trimethylpropyltin		131.7				2.4	8.8
SnCl <sub>4</sub> Stannic chloride	-30.2	113.0				5.2	18
TiCl <sub>4</sub> Titanium tetrachloride	-30	136.0				2.7	9.2
Zn(CH <sub>3</sub> ) <sub>2</sub> Zinc dimethyl	-29.2	44				124	302
Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Zinc diethyl	-28	118.0				5.0	16
Zn(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Zinc dipropyl	-81 to -84	139.4				1.9	6.4
Zn(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Zinc dibutyl	-57.7	201.1					0.9





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